COMBUSTION

AND

FLAME

QUARTERLY JOURNAL OF THE COMBUSTION INSTITUTE

VOLUME I

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COMBUSTION & FLAME

Quarterly Journal of The Combustion Institute

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BUTTERWORTHS SCIENTIFIC PUBLICATIONS

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COMBUSTION & FLAME

Quarterly Journal of The Combustion Institute

Editorial Fire has been man's fierce ally throughout his struggle for existence and ascendency. Fire is now man's slave—rebellious and mysterious—enabling his most daring designs to be constructed and his most bold adventures to be achieved.

The taming of this mighty creature—the understanding of the nature of combustion and flame—has only come about in the last hundred and fifty years. The development of the paraphernalia of modern civilization—modern boilers, industrial furnaces, internal combustion engines and gas turbines, rockets *etc*—has gone hand in hand with the growth of knowledge of thermal energy and of its liberation by combustion. There is still much that is unknown, much that cannot be formulated in exact mathematical language, and therefore much that is still of interest to the experimentalist. There is indeed much to keep the scientist busy in the realm of combustion and flame for many a long year; the chemical reactions which are taking place in flames of different combustible gases are complex and, as yet, imprecisely known, and the transfer of mass and of heat in the many different kinds of combustion equipment are often unpredictable.

There has been no journal specially adapted for the publication of scientific papers in the field of combustion and flame. The papers have appeared in journals relating to Fuel, to Aeronautics, to Metallurgy, to Oil Technology, to Physics and Physical Chemistry—in fact 'all over the place'. Some members of The Combustion Institute, which is now responsible for the Symposia on Combustion which have been held biennially in recent years, felt that there was need for a Journal of Combustion and Flame in which scientific work on the subject could be published. The Institute is organized on an international basis and the Journal is also being so established. *Fuel*, a Journal of Fuel Science, published by Butterworths, London, was already well established as an international journal for fuel and an increasing number of communications on combustion were being published in that Journal, but the subject is so wide that it was agreed that two journals were needed, one for Fuel and one for Combustion and Flame. It was further agreed that the new Journal for Combustion and Flame should be the official journal of The Combustion Institute and have an Editorial Board appointed by agreement between the publishers and the Institute, with an Editor for the British Commonwealth, Europe and Asia and an Editor for the United States. It was further agreed that a combined subscription to both the journals *Fuel* and *Combustion and Flame* should be available at a reduced rate.

Fuel continues as a Journal of Fuel Science published by Butterworths, and both journals for the present come under my general editorship.

Dr. Bernard Lewis has accepted the United States editorship for *Combustion and Flame* and Professor A. R. Ubbelohde the editorship on this side of the Atlantic*.

Papers on combustion for the new journal from countries other than the United States should be sent to Butterworths, 4-5 Bell Yard, Temple Bar, London, W.C.2, and papers from the U.S.A. to The Combustion Institute, Union Trust Buildings, Pittsburgh 19, Pennsylvania. If some papers submitted to the Journal are considered by the Editors as falling in the field of fuel science rather than combustion, they may be transferred, with the author's consent, to *Fuel*, similarly with papers submitted to *Fuel* which are more suitable for *Combustion and Flame*. The decision as to such transfer rests with the General Editor.

An insert to this issue gives instructions to guide authors in the details relating to the presentation of their communications.

The new Journal is a journal of combustion science and it is not intended to publish papers on plant or process, or such matters of a technical and engineering character which do not relate to underlying scientific principles but are merely descriptive or are concerned with details of operation. However, methods of experimentation and analysis which help to elucidate the scientific principles of combustion or flame would not be outside the range.

We shall hope to receive papers from the many laboratories which are interested in the application of the scientific principles of combustion and are carrying out research on the subject, whether it be in relation to aircraft, to boilers, to furnaces, to burners or whatever it may be. Likewise, papers on the structure and properties of flames—their propagation, spectroscopic analysis, constitution, ionization and so on—will be welcome, together with those on the kinetics of oxidation in the vapour state and other combustion reactions. Combustion within liquids and at the surfaces of solids are also within the range and would be fit subjects for papers in the Journal.

A. C. Egerton

*Some papers published in this first number had already been accepted for publication in *Fuel* and, with the agreement of the authors, were withheld for publication in the first number of this new Journal. After this, all papers from the United States will be collected by the U.S. Editor, Dr. Bernard Lewis, who will arrange for their review before being sent to London.

Stability Limits of Flames of Ternary Hydrocarbon Mixtures

P. F. KURZ

Studies of lean blow-off and flash-back limits of laminar flames of ternary hydrocarbon mixtures containing ethylene show that these stability limits of the mixtures are predictable. The fuel components are non-interfering in flames at these limits. The contributions of the individual hydrocarbons are additive and define the limit of the mixture. However, at rich blow-off, there is evidence of inhibition in mixtures where ethylene is the primary fuel and in mixtures where the ethylene concentration exceeds a certain minimum as a secondary fuel. Consequently, the rich blow-off limits of mixtures containing ethylene are not usually predictable.

THIS paper describes the behaviour of ternary mixtures of ethylene, propane, and *iso*butane at the lean and rich blow-off limits and at flash-back on a Bunsen flame shielded by an inert gas. Laminar flames only were studied. Data are presented to show the behaviour of each of the component fuels burning in a binary mixture with air, and these results are used to interpret the data obtained when ternary fuel mixtures burning with air were studied. Each component of the ternary mixture was used in turn as the primary fuel. The data for lean blow-off and for flash-back are shown to be in good agreement with the requirements of an empirical summation based on the additivity of the contributions of the individual components in the mixture, namely $\Sigma V_a/V_a^* = 1$. At rich blow-off in ternary mixtures in which ethylene is the primary fuel, a deviation from unity is found. This is attributed to the abnormal behaviour of ethylene when burning alone. The data obtained for lean blow-off substantiate the results of experiments with ternary hydrocarbon mixtures obtained earlier in lean blow-off studies of non-laminar flames on a vortex burner[1].

APPARATUS

Figure 1 is a diagram of the 1·75 cm Bunsen burner used in the experiments with ternary hydrocarbon mixtures. An annular stream of inert gas surrounding the burner tube excluded ambient atmospheric air from the environs of the burner port, and critical-flow orifices were used to meter the air and fuel flow rates; thus the inert gas stream served the same purpose as does a Smithells tube. Other work as yet unpublished has shown that changing the flow rate of the shielding gas influences the lean blow-off limit but does not appreciably affect the other stability limits. Accordingly, in the present work, the flow rate of the shielding gas was held constant so that it would have essentially the same influence upon all fuel mixtures at any given air flow rate. Consequently, the limits of the different fuel mixtures at a given air rate could confidently be compared. The operation of the mixing system, the provisions for straightening the flow, the method of introducing

and controlling the flow of gas in the flame-shielding mantle, and the provisions for quenching flash-back have been described earlier[2].

The rim of the burner port is kept at a uniform temperature by circulating water from a sump through the burner jacket. The components of the mixing system and the gas delivery lines are immersed in the water in the sump.

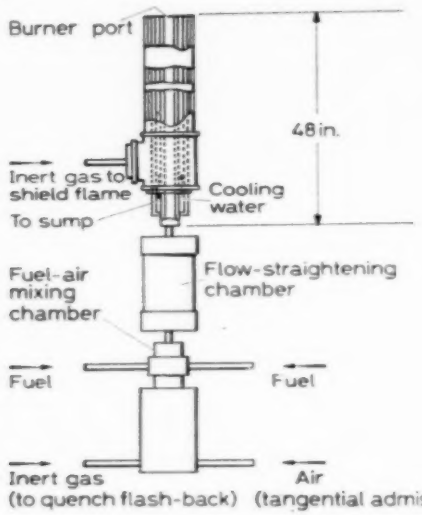

Figure 1. Schematic diagram of Bunsen burner shielded by inert gas, and mixing system

EXPERIMENTAL PROCEDURE

To observe stability limits, the flow of inert gas (nitrogen) in the mantle was adjusted to produce an average velocity of about 30 cm/sec in the annulus. The air flow through the burner was set at about 5 l./min and fuel was then admitted until a stable lean flame was produced. When more than one fuel was used, as in the experiments with ternary mixtures, the flow rates of two of the fuels, designated as the secondary fuels, were set at predetermined values and were held constant throughout the experiment. The third component of the fuel mixture was designated as the primary fuel, and its flow was changed as required to reach the desired stability limit, *e.g.* lean blow-off, flash-back, or rich blow-off. The remainder of the experimental procedure has been described in detail elsewhere[2].

In the experiments with ternary hydrocarbon mixtures each of the component fuels was used in turn as the primary fuel. Compressed air from commercial cylinders was used to maintain close control over the driving pressure in the air lines at all times.

EXPERIMENTAL RESULTS

Stability limits of single hydrocarbon–air flames

Figure 2 compares the lean and rich blow-off limits of ethylene–air, propane–air, and *iso*butane–air flames on the 1·75 cm Bunsen burner. The

abscissa scale is in units of equivalent ethylene in order that the behaviour of the fuels may be compared directly on a basis of their relative oxygen requirements. *Figure 2* shows that the blow-off limits of ethylene, the

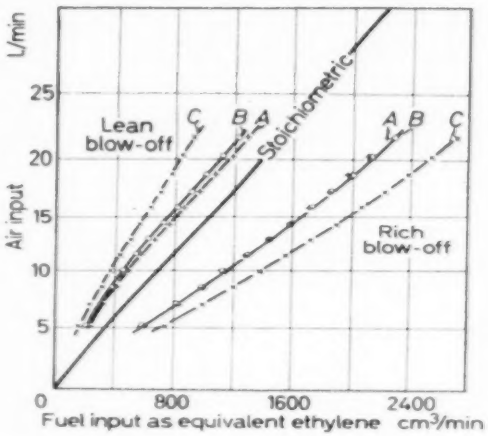

Figure 2. Blow-off limits of laminar hydrocarbon–air flames on a nitrogen-shielded burner: A isobutane; B propane; C ethylene

fastest burning of these three hydrocarbons, are considerably wider than those of propane or of *iso*butane. Lean propane flames are shown to be slightly more stable than lean *iso*butane flames. However, propane and *iso*butane flames have about the same rich limit on the fuel equivalent scale.

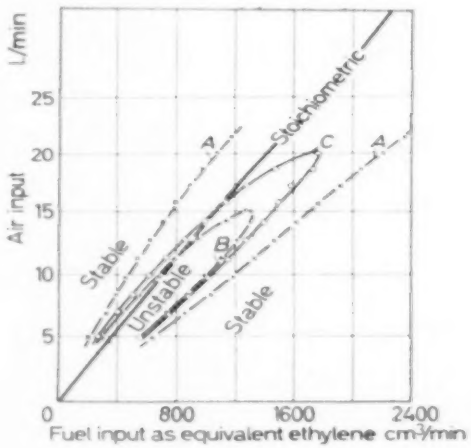

Figure 3. Flash-back limits of laminar hydrocarbon–air flames on a nitrogen-shielded burner: A ethylene; B isobutane; C propane

Figure 3 compares the flash-back limits of ethylene–air, propane–air, and *iso*butane–air flames on the 1·75 cm Bunsen burner. Ethylene has the widest region of instability, and *iso*butane the narrowest.

Stability limits of binary hydrocarbon–air flames

The behaviour of binary fuel mixtures of *iso*butane and ethylene burning with air on the inert-shielded Bunsen burner has been described in detail

elsewhere[2]. It was found that, when ethylene is the primary fuel in the binary mixture, the stability limits essentially parallel the corresponding limits for ethylene–air flames. Similarly, when *iso*butane is the primary fuel, the stability limits for the binary mixture are approximately parallel to the corresponding limits for *iso*butane–air flames.

The experimental stability data for these binary fuel mixtures were tested for agreement with an empirical summation, based on earlier work by H. LE CHATELIER[3] on flammability limits and by W. PAYMAN[4] and H. F. COWARD and H. P. GREENWALD[5] on flame speed, which may be written as

$$V_1/V_1^* + V_2/V_2^* = 1 \qquad \ldots\ldots [1]$$

where V_1 and V_2 are the volumetric inputs of fuels No. 1 and No. 2 in a binary mixture at a given stability level, *e.g.* an air input rate of 10 l./min at blow-off or at flash-back. V_1^* and V_2^* are the volumetric inputs of the single fuels No. 1 and No. 2 in their binary mixtures with air at the same selected stability level, *i.e.* an air rate of 10 l./min.

Figure 4 shows that when $V_{C_2H_4}/V_{C_2H_4}^*$ and $V_{C_4H_{10}}/V_{C_4H_{10}}^*$ are plotted against each other, a linear relationship is obtained for the lean blow-off data. Flash-back data likewise give a linear relation between V_1/V_1^* and V_2/V_2^*.

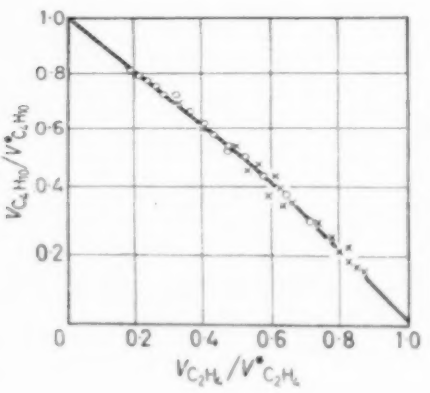

Figure 4. Relationship between $V_{C_2H_4}/V_{C_2H_4}^*$ and $V_{C_4H_{10}}/V_{C_4H_{10}}^*$ for isobutane–ethylene flames at lean blow-off on a nitrogen-shielded burner: primary fuels— isobutane; × ethylene

Accordingly, the equation

$$V_{C_4H_{10}}/V_{C_4H_{10}}^* + V_{C_2H_4}/V_{C_2H_4}^* = 1 \qquad \ldots\ldots [2]$$

is satisfied and the fuels are non-interfering in flames.

Figure 5 shows that at rich blow-off the stability-limit data for *iso*butane–ethylene mixtures were found to deviate slightly but regularly from linearity, so that at the rich limit $\Sigma V_a/V_a^* \neq 1$ but is slightly less than unity. This deviation at the rich limit has also been found in experiments with several other binary hydrocarbon mixtures containing ethylene as one of the fuels[6]. The deviation is believed to occur because values obtained for $V_{C_2H_4}^*$ are higher than would be predicted from the behaviour of other hydrocarbons. The abnormal behaviour of ethylene probably results from the occurrence

of thermal cracking reactions in ethylene flames near and at the rich blow-off limit. These reactions enhance the stability of rich ethylene flames and thereby extend the rich limit abnormally. Consequently, the presence of a fuel which burns less stably, such as *iso*butane, in a binary fuel mixture with ethylene permits the binary mixture to burn stably only in less rich

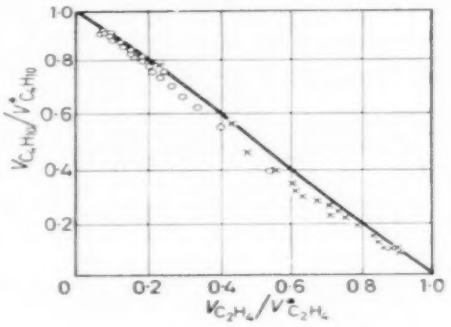

Figure 5. Relationship between $V_{C_2H_4}/V_{C_2H_4}^*$ *and* $V_{C_4H_{10}}/V_{C_4H_{10}}^*$ *isobutane–ethylene mixtures at rich blow-off on a nitrogen-shielded burner: primary fuels—o isobutane; × ethylene*

regions of fuel–air composition. In these regions of composition, the cracking reactions normally present in ethylene flames will not occur in the binary mixture and, as a result, the rich blow-off limit is narrower than would be predicted from a consideration of the blow-off limits of the component fuels, so that, for binary fuel mixtures containing ethylene, the values of $\Sigma V_a/V_a^*$ are less than unity at the rich blow-off limit.

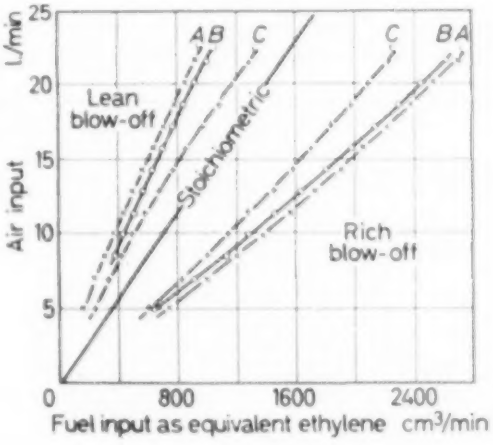

Figure 6. Blow-off limits of ethylene, isobutane, and ethylene–isobutane–propane flames on a nitrogen-shielded burner—primary fuel ethylene: A ethylene; B ternary fuel mixture; C isobutane

Ternary fuel mixture

Fuel	*Flow rate*
Propane	*60 ml/min*
Isobutane	*78 ml/min*
Ethylene	*Varied to establish limit*

Stability limits of ternary hydrocarbon–air flames

The ternary hydrocarbon systems which were studied contained ethylene, *iso*butane and propane. Each component fuel was used in turn as the primary fuel, *i.e.* as the one whose flow rate was changed to produce the desired effect, namely, lean blow-off, flash-back, or rich blow-off.

Figure 6 shows the lean and rich blow-off limits observed with ethylene, *iso*butane, and ethylene–*iso*butane–propane flames over a range of air rates

ranging from 5·0 to 21·6 l./min on the 1·75 cm Bunsen burner shielded with nitrogen to exclude ambient air. The primary fuel in this ternary mixture being ethylene, the stability curves for the mixture parallel the corresponding curves for ethylene flames, as would be expected.

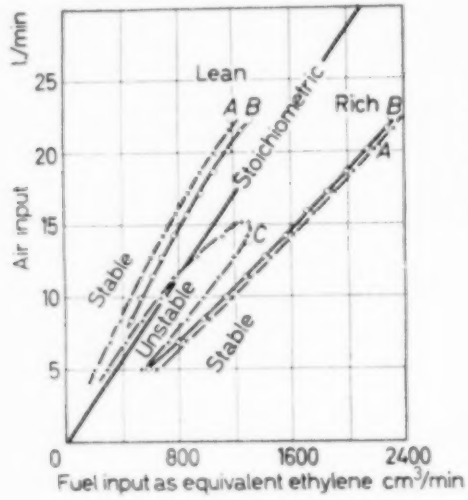

Figure 7. Flash-back limits of ethylene, isobutane, and ethylene–isobutane–propane flames on a nitrogen-shielded burner—primary fuel ethylene: A ethylene; B ternary fuel mixture; C isobutane

Ternary fuel mixture

Fuel	*Flow rate*
Propane	*60 ml/min*
Isobutane	*78 ml/min*
Ethylene	*Varied to establish limit*

Figure 7 shows the flash-back limits for ethylene, *iso*butane and ethylene–*iso*butane–propane flames on the nitrogen-shielded Bunsen burner. The curves for the ternary mixture parallel the limit curves for ethylene, as would be expected.

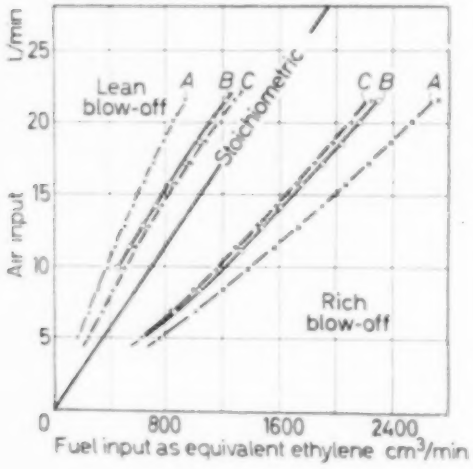

Figure 8. Blow-off limits of ethylene, isobutane, and isobutane–ethylene–propane flames on a nitrogen-shielded burner—primary fuel isobutane: A ethylene; B ternary fuel mixture; C isobutane

Ternary fuel mixture

Fuel	*Flow rate*
Propane	*60 ml/min*
Ethylene	*112 ml/min*
Isobutane	*Varied to establish limit*

Figure 8 shows the lean and rich blow-off limits for ethylene, *iso*butane, and *iso*butane–ethylene–propane flames in which *iso*butane is the primary fuel. The stability curves for the mixture parallel corresponding curves for *iso*butane flames, as would be expected.

Figure 9 shows flash-back limits for ethylene, *iso*butane, and *iso*butane–ethylene–propane flames over a range of air rates. The flash-back peninsula for the ternary mixture is closed at the top and essentially parallels the flash-back peninsula for *iso*butane flames, although, to be sure, the range of the flash-back peninsula is extended to higher air rates when ethylene

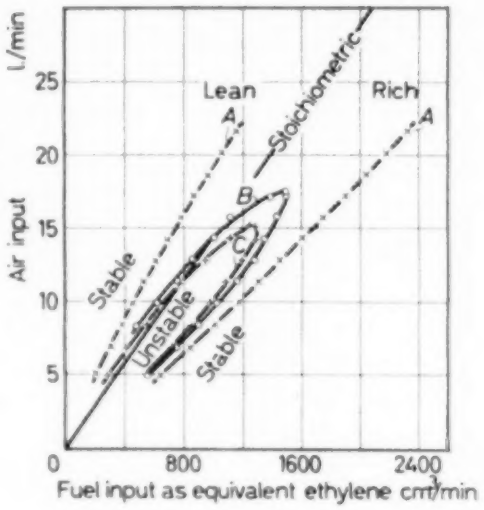

Figure 9. Flash-back limits of ethylene, isobutane, and isobutane–ethylene–propane flames on a nitrogen-shielded burner—primary fuel isobutane: A ethylene; B ternary fuel mixture; C isobutane

Ternary fuel mixture

Fuel	*Flow rate*
Propane	*60 ml/min*
Ethylene	*112 ml/min*
Isobutane	*Varied to establish limit*

and propane are present. This is to be expected as both ethylene and propane will tend to extend the flash-back limits of a mixture whose primary fuel is *iso*butane.

Figure 10 shows the lean and rich blow-off limits of ethylene, propane, and propane–*iso*butane–ethylene flames over a range of air rates on the shielded 1·75 cm Bunsen burner. Propane is the primary fuel in this ternary fuel mixture. The stability curves for the ternary mixture parallel

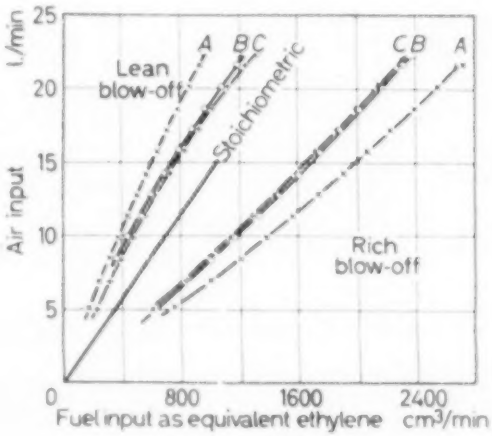

Figure 10. Blow-off limits of ethylene, propane, and propane–isobutane–ethylene flames on a nitrogen-shielded burner—primary fuel propane: A ethylene; B ternary fuel mixture; C propane

Ternary fuel mixture

Fuel	*Flow rate*
Ethylene	*112 ml/min*
Isobutane	*52 ml/min*
Propane	*Varied to establish limit*

the corresponding curves for propane flames, as would be expected, and, furthermore, they lie fairly close to the curves for propane flames because propane is the 'median' fuel. Whereas the presence of ethylene tends to widen the limits of the mixture, the simultaneous presence of *iso*butane tends to narrow the limits and so a rather 'neutral' effect results.

Figure 11 shows the flash-back limits of ethylene, propane, and propane–*iso*butane–ethylene flames on the 1·75 cm burner. The flash-back curve for the ternary mixture parallels closely the corresponding curve for propane flames. As in the instance of the blow-off limits, the flash-back data show the rather 'neutral' effect on the ternary mixture when propane is the primary fuel and ethylene and *iso*butane are present in approximately equal amounts as regards oxygen requirement. The counteracting influences of ethylene and *iso*butane are well illustrated by the data shown in *Figures 10* and *11*.

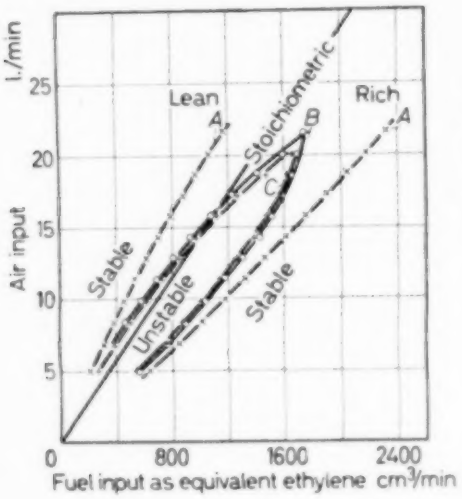

Figure 11. Flash-back limits of ethylene, propane, and propane–isobutane–ethylene flames on a nitrogen-shielded burner—primary fuel propane: A ethylene: B ternary fuel mixture: C propane

Ternary fuel mixture

Fuel	*Flow rate*
Ethylene	*112 ml/min*
Isobutane	*52 ml/min*
Propane	*Varied to establish limit*

Values of V_a/V_a^* were calculated for the components of the ternary mixtures, and the data were examined by plotting V_1/V_1^* as the abscissa, to represent the primary fuel, and $V_2/V_2^* + V_3/V_3^*$ as ordinate, to represent the two secondary fuels. Because $\Sigma V_a/V_a^* = 1$ when the fuels are entirely

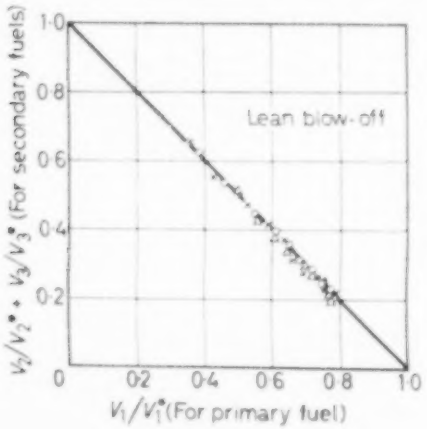

Figure 12. Relationship between V_1/V_1^* and $V_2/V_2^* + V_3/V_3^*$ for ternary mixtures of ethylene, isobutane, and propane at lean blow-off: primary fuels—o propane: × ethylene: △ isobutane

compatible, a linear relationship between V_1/V_1^* and $(V_2/V_2^* + V_3/V_3^*)$ shows agreement with equation 1. Linear relationships were found for the lean blow-off limit and for the flash-back limit; they are shown in *Figures 12* and *13* respectively.

At rich blow-off, however, a slight inhibiting influence is indicated. When the data for all three ternary mixtures at rich blow-off are plotted on a single graph, only a general trend is shown. When the results for the

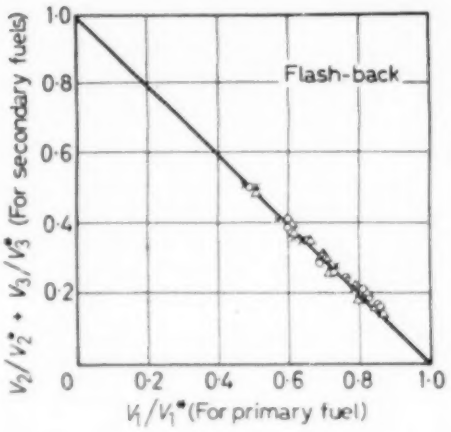

Figure 13. Relationship between V_1/V_1^* *and* $V_2/V_2^* + V_3/V_3$ *for ternary mixtures of ethylene, isobutane, and propane at flash-back: primary fuels—× ethylene; o propane; △ isobutane*

three ternary mixtures are examined separately, however, a clearer indication of inhibition is given, as shown in *Figures 14, 15* and *16* in which the primary fuels are ethylene, propane and *iso*butane respectively.

Figure 14 shows that the secondary fuels, propane and *iso*butane, which burn more slowly than ethylene, inhibit somewhat the stability of ethylene at the rich blow-off limit. With these saturated hydrocarbons a less rich

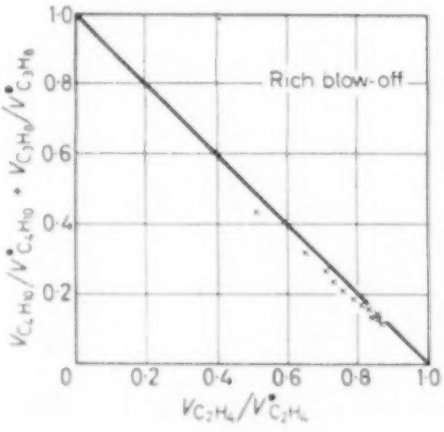

Figure 14. Relationship between $V_{C_2H_4}/V_{C_2H_4}^*$ *and* $V_{C_4H_{10}}/V_{C_4H_{10}} + V_{C_3H_8}/V_{C_3H_8}$ *at rich blow-off—primary fuel ethylene*

mixture is required to achieve stability and thus create interference with the thermal cracking reactions which ethylene normally exhibits near and at the rich limits. Accordingly, the rich limit of the ternary mixtures is narrowed slightly, thus requiring less ethylene, the primary fuel, to cause rich blow-off. Consequently the value of $V_{C_2H_4}/V_{C_2H_4}^*$ is decreased and $\Sigma V_a/V_a^*$ is consistently less than unity for these mixtures; it ranges from 0·95 when $V_{C_2H_4}/V_{C_2H_4}^*$ has a value of 0·51, to 0·99 when $V_{C_2H_4}/V_{C_2H_4}^*$ is about 0·85 or greater, *i.e.* $\Sigma V_a/V_a^*$ approaches unity as $V_{C_2H_4}/V_{C_2H_4}^*$ approaches unity.

Figures 15 and *16* show a deviation from unity of −0·03 and −0·01 respectively, only when values of $V_{C_2H_4}/V_{C_2H_4}$ exceed 0·11. When $V_{C_2H_4}/V_{C_2H_4}^*$ is less than 0·10 the values $\Sigma V_a/V_a^*$ are unity for the mixtures containing *iso*butane or propane as the primary fuel. This is consistent with the data given in *Figure 14* where ethylene is the primary fuel.

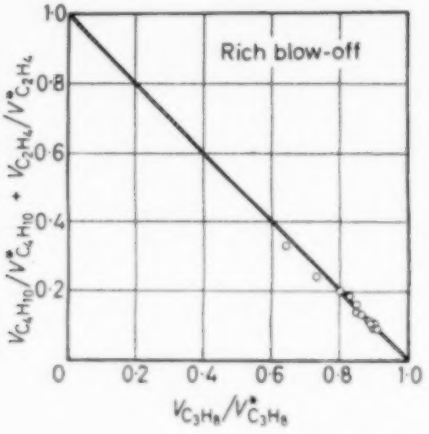

Figure 15. Relationship between $V_{C_3H_8}/V_{C_3H_8}^*$ *and* $V_{C_4H_{10}}/V_{C_4H_{10}}^* + V_{C_2H_4}/V_{C_2H_4}^*$ *at rich blow-off for ternary mixtures—primary fuel propane*

DISCUSSION

It has been shown in the foregoing sections that shielded flames of ternary hydrocarbon mixtures behave like those of similar flames of binary mixtures at lean blow-off and at flash-back in the region of laminary flow on a 1·75 cm Bunsen burner. It has also been shown that the experimental data

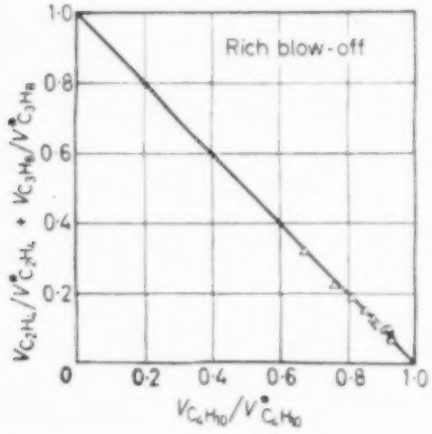

Figure 16. Relationship between $V_{C_4H_{10}}/V_{C_4H_{10}}^*$ *and* $V_{C_3H_8}/V_{C_3H_8}^* + V_{C_2H_4}/V_{C_2H_4}^*$ *at rich blow-off for ternary mixtures—primary fuel isobutane*

for binary and ternary mixtures at the lean blow-off and the flash-back limits are in agreement with the requirements of an empirical equation, namely,

$$V_1/V_1^* + V_2/V_2^* + V_3/V_3^* = \Sigma V_a/V_a^* = 1 \quad \ldots\ldots[3]$$

It therefore seems reasonable to conclude that, at lean blow-off and at flash-back, equation 3 may be generalized for any mixture of hydrocarbons containing n components, as follows

$$\frac{V_1}{V_1^*} + \frac{V_2}{V_2^*} + \cdots\cdots \frac{V_n}{V_n^*} = \sum_{a=1}^{n} \frac{V_a}{V_a^*} = 1. \quad \ldots\ldots[4]$$

Accordingly, if the behaviours of all of the components of a multi-hydrocarbon mixture are known, the behaviour of the mixture can be predicted. Similarly, if the behaviours of the mixture and of all but one of its components are known, the behaviour of this one component can be predicted.

At rich blow-off with ternary mixtures which contain ethylene as one of the fuel components, there is a slight deviation from the requirements of equation 3 and $\Sigma V_a/V_a^*$ is found to be less than unity. This is attributed to the interference of saturated hydrocarbons with the thermal cracking reactions which ethylene undergoes near and at the rich limit, so the net result is that the rich limit of the ternary mixture is narrowed more than would be expected from a consideration of the rich limits of the component fuels. It is therefore concluded that ternary mixtures containing ethylene show a slight but consistent inhibiting effect at the rich limit.

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The Ignition of Dust Layers on a Hot Surface

K. N. PALMER and P. S. TONKIN

The ignition temperatures of dusts have been measured by depositing dust layers on a hot surface at controlled temperatures. The application of the method to practical problems is considered.

A COMBUSTIBLE dust deposited on a solid surface may ignite if the temperature of the surface is sufficiently high. The ignition of dusts by this means can lead to fires, and hence a knowledge of the ignition temperatures of the dusts would be of assistance in taking effective measures to prevent such fires. Unfortunately, in spite of a considerable amount of experimental investigation by many workers, it is not yet possible to define the ignition temperature solely in terms of the properties of the dust, and so, when values of ignition temperatures are required in connection with a practical problem, the method of their measurement should be as similar as possible to the heating process envisaged in practice. The present experiments were therefore carried out by depositing the dusts on a hot plate at controlled temperatures and measuring the minimum temperatures of the plate at which ignition occurred. These minimum temperatures were taken to be the ignition temperatures of the dusts. Brief accounts have been given of the use of a similar technique for determining the ignition temperatures of layers of coal dust[1, 2], and details have also been given of the measurement of the rise in temperature caused by the insulating effect of layers of coal dust deposited on a surface to which heat is supplied at a constant rate.

EXPERIMENTAL

Materials

Several dusts were tested and some characteristics of each are given in *Table 2*. The cork dust and mixed wood sawdust were chosen as being typical common industrial dusts and the coal dust was included for comparison with the earlier experiments mentioned above[1, 2]. The carbonized sawdust had been obtained from previous experiments on smouldering combustion, described elsewhere[3], in which a deep layer of the mixed wood sawdust was ignited by a buried source of ignition. The resulting smouldering combustion formed the carbonized material which was removed when hot and allowed to cool in sealed tins.

Apparatus

The hot plate was constructed from an ordinary commercial 1 kW boiling plate by removing the original heating surface and replacing it with a heavy

steel plate 19·1 cm in diameter and 1·25 cm thick. A *Chromel–Alumel* thermocouple was soldered to the upper surface of the plate and the leads were taken through the plate and connected by way of a battery circuit and a d.c. amplifier to a relay switch controlling the heating current. With this automatic system the temperature of the upper surface of the plate could be maintained within ±4° C of a pre-determined value, irrespective of whether the plate was covered with dust.

The dusts were either deposited on the plate as flat-topped conical heaps, whose dimensions are given in *Table 1*, or rested on the plate inside a vertical cylindrical metal sleeve of diameter 17·9 cm. The metal sleeve was used only in experiments on the variation of the ignition temperature with the depth of the dust layer.

Table 1. Dimensions of the dust heaps

Vertical depth cm	*Diameter of top cm*	*Diameter of base cm*
2·5	3·5	9·0
5·0	7·5	17·8

Procedure

The plate was heated to the temperature required for the experiment and the dust was weighed out and deposited on the plate either from a mould or within the metal sleeve. The packing densities of the dusts are listed in *Table 2*. The time was then recorded between the deposition of the dust on the plate and the appearance of smouldering combustion on the upper surface of the dust layer. With each dust and after each ignition, the temperature of the plate was lowered by 10° C until a temperature was reached at which ignition did not take place within a prolonged period, which was at least several hours and was sometimes overnight.

Table 2. The ignition temperatures of dusts in conical heaps

Dust	*Particle diameter cm*	*Packing density of dust g/ml*	*Ignition temperature °C*	
			Dust depth 2·5 cm	*Dust depth 5·0 cm*
Cork	<0·0065	0·17	260	—
Cork	0·043	0·08	280	—
Cork	0·38	0·07	320	260
Mixed wood sawdust	0·14	0·20	270	240
Carbonized wood sawdust	—	0·20	240	210
Coal dust (Dalton Main dull coal)	<0·0063	0·47	210	—

Results

The ignition temperatures of a range of dusts in conical heaps are shown in *Table 2*; the results also show the variation of the ignition temperature of cork dust with the particle size.

The variation of the ignition temperatures of the dusts with the thickness of the deposit was investigated in detail with wood sawdust and the results

are given in *Table 3*, which also shows the times required for smouldering combustion to emerge on the surface of the dust layer.

Table 3. Variation of the ignition temperature of wood sawdust with the thickness of the deposit

Depth of dust cm	*Ignition temperature °C*	*Time between formation of layer and appearance of smouldering h*
2·5	270	0·85
5·0	240	3·6
7·5	230	7·0
10·0	230	7·5
12·5	220*	13·8

*Not tested at plate temperatures below 220 C

DISCUSSION

Ignition temperatures of various dusts

The coal dust had the lowest ignition temperature (210 C) of any of the dusts tested in layers 2·5 cm in depth, but this temperature was higher than the 190 C reported elsewhere[1] for a coal dust of similar particle size. However, the two coals tested were not identical, being Dalton Main dull coal and Silkstone coal[1] respectively, and the discrepancy in the ignition temperatures may be due to the differences in the types of coal.

The ignition temperatures of carbonized wood sawdust, listed in *Table 2*, were 30 C less than the corresponding values for the original sawdust and it is of course possible that pre-carbonizing under different conditions from those in the present experiments could cause greater reductions in the ignition temperature; further investigation of this point is needed.

The ignition temperatures given in *Tables 2* and *3* were determined with a surface maintained at a constant temperature for experimental convenience, but in applying the results to practical cases the possibility should be taken into account that the deposition of a layer of dust may permit the temperature of the underlying surface to increase, as mentioned in the introductory paragraph. The extent of the increase in temperature would of course depend on the rate of supply of heat and other local conditions.

Variation of ignition temperature with particle size

The ignition temperature of cork dust increased with the particle size, but the effect was not great. Thus a decrease of 60 C in the ignition temperature, caused by a large reduction in the particle size, could also be obtained by increasing the depth of the dust layer from 2·5 to 5·0 cm (*Table 2*).

Variation of ignition temperature with depth of layer

The ignition temperature of mixed wood sawdust fell as the depth of the dust layer on the hot plate increased, and the time required by the smouldering combustion to reach the top surface of the layer increased appreciably (*Tables 2* and *3*). Coal dust behaved in a similar manner, as reported elsewhere[1]. Identical values were found for the ignition tempera-

ture of a given depth of mixed wood sawdust irrespective of whether the dust was in a conical heap or was contained in a metal sleeve on the hot plate.

The lowest ignition temperature that can be attained by increasing the depth of a given dust is important in fire prevention and estimations of minimum ignition temperatures have therefore been made by extrapolation, as shown in *Figure 1*. The relation between the ignition temperature and

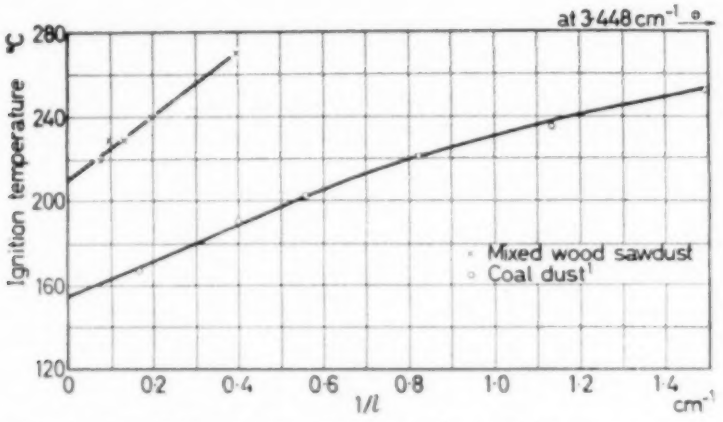

Figure 1. The relation between the ignition temperature and the depth of dust (l)

$1/l$, where l is the depth of the dust layer, is approximately linear for both mixed wood sawdust and for coal dust but breaks down for coal dust layers less than 1 cm deep. The minimum ignition temperatures, obtained by extrapolation to $1/l = 0$, are 210 °C for mixed wood sawdust and 155 °C for coal dust. Such minimum values are of course only valid for dust deposits in conditions similar to those used in the experiments, the base of the layer being heated and the top of the layer exposed to the atmosphere.

As there is evidence that the ignition temperature of dusts can be reduced by pre-carbonizing it is clear that the minimum ignition temperatures determined by the above method can only apply to the dusts in the condition tested. In practice, if dust accumulations are liable to undergo thermal decomposition, the maximum permissible surface temperature ought to be well below that recommended for the original dust, unless tests on the decomposed material show a reduction to be unnecessary.

CONCLUSIONS

The ignition temperature of dust layers on a hot surface decreased as the particle size of the dust was reduced.

The ignition temperature also fell when the depth of the dust layer was increased, and appeared to approach a limiting minimum value, in agreement with the results of other workers. A method of estimation of minimum ignition temperatures is described.

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Herts

(*Received January 1956*)

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A Photoelectric Study of the Light Emission from Carbon Monoxide–Oxygen Thermal Explosions

A. S. GORDON, A. L. BENNETT and N. DAVIDSON*

A study of the time and space dependence of the visible plus ultra-violet light output of a carbon monoxide–oxygen thermal explosion in a quartz bulb shows that the combustion process originates in the hottest region of the bulb and propagates as a flame throughout it. The light build-up and fall-off is much slower than for hydrogen–oxygen explosions, as is the flame velocity. The light yield of a stoichiometric mixture at a fixed partial pressure is increased by addition of carbon monoxide and decreased by addition of oxygen. The total light output of a mixture containing $2CO:2O_2$ *is the same at 147 mm and at 250 mm and is decreased by addition of carbon dioxide or water.*

THE TOTAL light emission of a carbon monoxide–oxygen flame has been investigated by H. KONDRATJEWA and V. KONDRATJEW[1-3]. They studied the effect of composition and pressure on brightness, using photometric methods, and concluded that the light yield was a maximum at 35 to 37 mm pressure and that both carbon monoxide and oxygen quench the light, oxygen being about five times as effective as carbon monoxide. The light was presumed to be due to emission by electronically excited carbon dioxide molecules.

B. W. BULLOCK and S. SILVERMAN[4] have studied the time variation of the pressure and the infra-red emission from spark ignited explosions in moist carbon monoxide–oxygen mixture.

In the present work, the light emission (in the wavelength range 2000 to 6000 Å) from thermal explosion of a carbon monoxide–oxygen mixture has been investigated by a photoelectric method. The time variation of the light intensity from two portions of the reaction vessel was recorded simultaneously and the presence of a combustion wave demonstrated. The dependence of light emission upon composition was studied.

APPARATUS AND PROCEDURE

Method 1—The mixture to be studied was admitted at low temperature to a spherical quartz reaction vessel, 10 cm in diameter and set in a furnace, and the furnace heated at a rate of 10° to 15°C/min until an explosion occurred. The light from the explosion was viewed through two holes in a metal plate at the top of the furnace. These holes were oriented so that the 1P28 photomultiplier tube received light through one aperture from a pencil traversing the reaction vessel vertically near its centre, and through the other from a larger pencil near the edge of the vessel. One light beam

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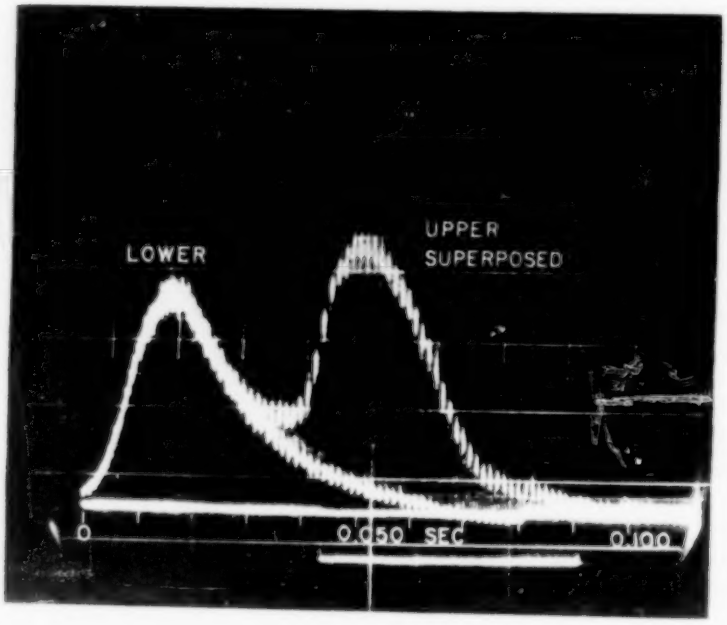

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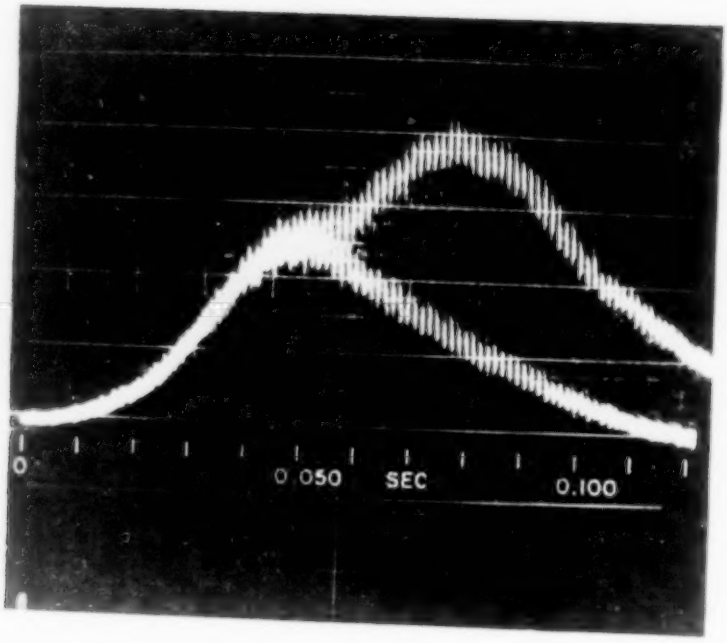
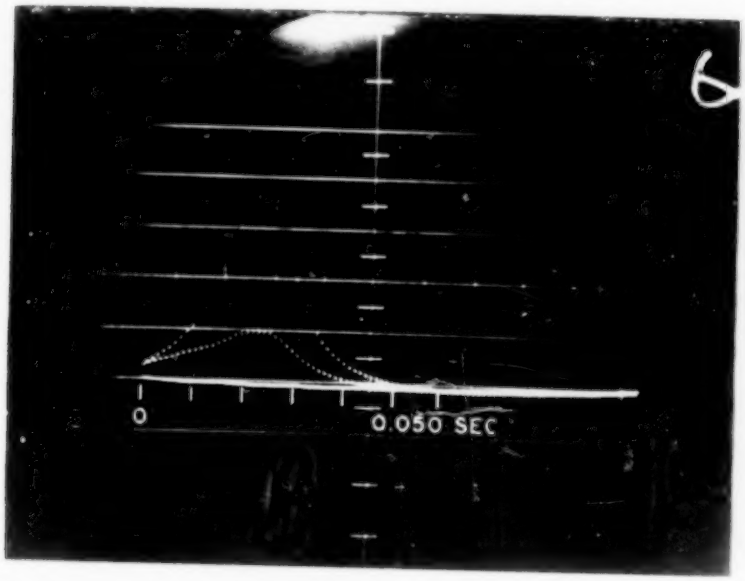


b

FIGURE 1. Photoelectric records of thermal explosions. a, Methyl-2-[ω-(2-pyridyl)-heptanoyl]-benzoate, 129 mm. at the explosion temperature of 548° C., sweep rate 0.012 sec. per cm., shape rate 0.0011 sec. per cm. b, Methyl-2-[ω-(2-pyridyl)-heptanoyl]-benzoate, 22 mm. at the explosion temperature of 548°.



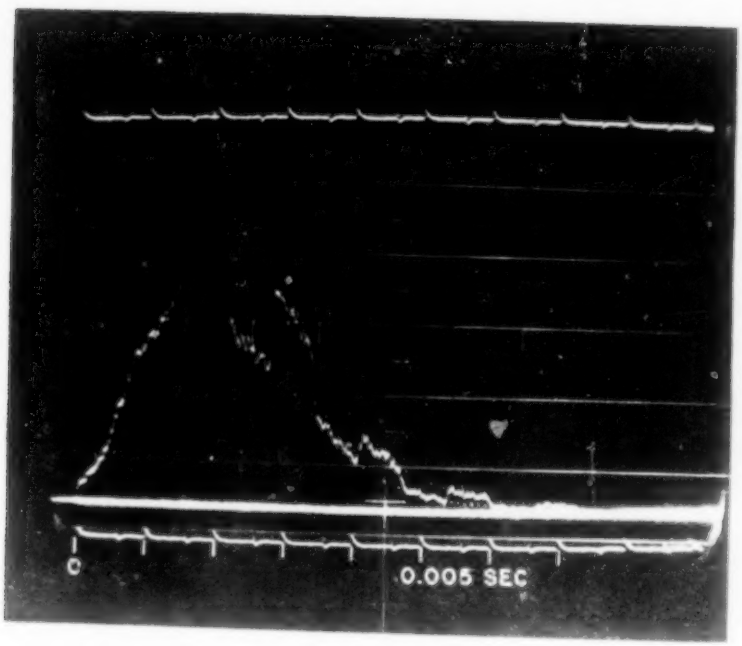


Figure 1. Photoelectric records of thermal explosions. *c*, Method 1, 1000 CO + oxygen, pressure 228 mm at the commencement of explosion, 24.1°C. *d*, method 3, 2H + CO + oxygen, pressure 67 mm at the commencement of explosion, 4.9°C. The photomultiplier has been screened and

was chopped to distinguish it from the other one. The photoelectric signals corresponded to a primary photocurrent of about 10^{-11} amp and were photographed from the oscillograph record.

Method 2—The object was to view two different horizontal positions in the reactor. A vertical cylindrical quartz cell 6 cm in diameter and 15 cm long was used. The light from the explosion was brought out of the furnace by two platinum mirrors on fused silica rods set so that they defined two horizontal pencils about 5 mm in diameter, each traversing a diameter of the reaction cell. One beam was 3·8 cm above the bottom of the vessel; the other was chopped and was 11·4 cm above the bottom.

Intensity measurements on duplicate runs were reproducible to ±10 per cent.

RESULTS AND DISCUSSION

A typical result obtained by Method 1 may be seen in *Figure 1c*. The light intensity curves show that the presence of the wall has no significant effect on the history of the light from the reaction. The shape of the curves indicates that the explosion may be initiated simultaneously in all regions of the reaction vessel, though this explanation is unlikely in view of the fact that there is a 15° gradient from the bottom to the top of the reaction vessel. An alternative explanation is that the chemical reaction which produces the light is so slow that the region where the explosion starts is still emitting light when a region 10 cm distant is emitting at maximum intensity. To check this explanation the experiments using Method 2 were performed. *Figure 1* is the time history of light from an explosion propagated from the bottom of a cylindrical reaction vessel. The light intensity from the first station is still about 25 per cent of its maximum when the light from the second station 3 in. from the first station is a maximum. It might be argued that the flame front is curved and not straight, as assumed in the above discussion. However, the light from the lower pencil in *Figure 1a* rises from 10 per cent to 100 per cent in a maximum of 0·012 sec and decays to 10 per cent in 0·035 sec. Since the combustion wave travels 7·6 cm in 0·035 sec, a curved flame front would have to have its apex 15 cm in front of its base to explain the experimentally observed duration of 0·070 sec. This is most unlikely in a cylinder of 6 cm diameter.

Figure 1d shows a record of the light output from an explosion in a $2H_2:1O_2$ mixture. There is only about 0·05 as much light and the flame velocity is about 200 times faster. The light rises and decays much more rapidly in each pencil. The temperatures reached in the $2CO:1O_2$ and the $2H_2:1O_2$ combustions are similar and the rates of cooling must be comparable. All these facts taken together indicate that in the carbon monoxide–oxygen explosion the light emission is due to chemiluminescence rather than thermal emission, and that the long duration of the light emission is due to the slow nature of the combustion process. It would appear that the flame front or reaction zone is 5 to 10 cm thick. The observation that the reaction velocity in pure and dry carbon monoxide–

oxygen mixtures is slow has been previously indicated in other experiments. For example, the fact that it has not yet been possible to establish a stable flame in a dry carbon monoxide–oxygen mixture, and the ease with which 'spin' sets in for detonations in dry carbon monoxide–oxygen mixtures are both due to the slow reaction velocity.

Comparison of *Figure 1a* and *1b* illustrates a phenomenon that was consistently observed; the flame velocity for a $2CO: 1O_2$ mixture is about the same as that for a $1CO: 2O_2$ mixture, but the duration of the light pulse from either station is much greater with the former. It is pointed out below that the total light output falls as the O_2: CO ratio increases. This ratio does increase during the combustion process for the $1CO: 2O_2$ mixture, thus providing a mechanism for quenching the light emission, whereas this ratio stays approximately constant during the combustion of stoichiometric $2CO: 1O_2$ mixture.

The observed flame velocities of about 220 cm sec^{-1} are due to two effects: propagation of the combustion wave, and mass flow due to the compression of the uncombusted gas. In view of this complexity a detailed quantative study of the velocity data is not warranted.

The integrated light output from each of the two beams is plotted in *Figure 2* as a function of percentage of carbon monoxide. With the one exception noted in the *Figure 2*, the experiments are at a constant partial

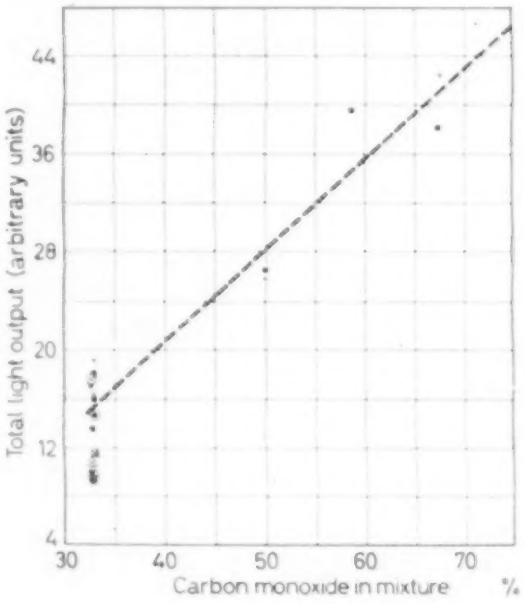


Figure 2. Integrated light output as a function of composition — unless otherwise specified, the partial pressure of stoichiometric mix is about 72 to 75 mm, and additional CO or O_2 are added as indicated: ● lower mirror; × upper mirror; △ 0·43 per cent H_2O; □ 16 per cent CO_2; ○ approximately doubled pressure

pressure of stoichiometric mix ($2CO: 1O_2$) of about 75 mm at 650° C with added carbon monoxide, oxygen, carbon dioxide or water. Since the total carbon dioxide formed varies little, the following qualitative conclusions may be drawn from this data:

(*1*) Addition of oxygen to the stoichiometric mix decreases the light yield (total light output/mole carbon dioxide formed)

(*2*) Addition of carbon monoxide increases the light yield

(*3*) Carbon dioxide decreases the light yield, and so does a small percentage of water

(*4*) When the pressure of a $1CO: 2O_2$ mix is changed from 147 to 250 mm Hg the light output is decreased slightly and thus the light yield is approximately halved.

The above observations are consistent with the main conclusions of the work of R. H. KNIPE and A. S. GORDON[5,6] on spectroscopic and second explosion limit studies of the carbon monoxide–oxygen reaction. Due acknowledgements for the important contributions of other investigators are made in these two papers.

The pertinent facts and hypotheses of these references are:

(*a*) An electronically excited state of carbon monoxide ($a^3\Pi_r$) has been detected in carbon monoxide–oxygen explosions

(*b*) 90 per cent or more of the light between 4000 and 6000 Å radiated by carbon monoxide–oxygen explosions is in the continuum background rather than in the 'flame bands'

(*c*) It is proposed that the continuum light is mainly due to the process $^3CO^* + {}^3O_2 \longrightarrow {}^3CO_3^*$, followed by either $^3CO_3^* \longrightarrow CO_2 + {}^3O + h\nu$ or by $^3CO_3^* \longrightarrow CO + {}^3O_2 + h\nu$

(*d*) The chain branching reaction is $^3CO_2^* + {}^3O_2 \longrightarrow CO_2 + {}^3O + {}^3O$, $^3CO_2^*$ being an excited triplet state of CO_2

(*e*) $^3CO^*$ is formed by $^3CO_2^* + CO \longrightarrow CO_2 + {}^3CO^*$

(*f*) Oxygen atoms are quenched termolecularly $CO + {}^3O + M \longrightarrow {}^3CO_2^{**} + M$ where CO_2^{**} is a low lying triplet state as proposed by A. D. WALSH[7].

The effect of carbon monoxide in increasing the light yield follows readily from these assumptions. The light quenching effect of oxygen is due to the reaction in *d*. The decrease in light yield with pressure is due to the increase in importance of the termolecular reaction *f* compared to the bimolecular reactions as pressure is increased.

The effect of small percentages of water in decreasing the light yield and increasing the ease of explosion is presumably due to a quenching reaction with one of the electronically excited species in which H and OH are formed. The light quenching effect of carbon dioxide is probably due to a reaction which quenches one of the electronically excited species.

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The Slow Oxidation of Methane—The Role of the Surface on the Course of the Oxidation of Methane

SIR A. C. EGERTON, G. J. MINKOFF AND K. C. SALOOJA*

Following the authors' investigation on the slow oxidation of methane and using methods previously described, the effects of surfaces of various kinds on the course of the reactions have been studied at temperatures from 450° to 500° C and pressures from 100 to 400 mm Hg. The amounts of the intermediates, formaldehyde and hydrogen peroxide, have been determined. The reactions are more rapid when carried out in silica vessels or in Pyrex *vessels treated with hydrofluoric acid and washed with water. In soda glass vessels or in vessels coated with potassium chloride or alkalis, the reaction proceeds much more slowly and with a long induction period; hydrogen peroxide is destroyed. In the treated vessels, the order of the reaction and the activation energy were found to be 2·3 and 39·3 kcal respectively. The effect on the reaction rate of size of vessel and of packing was determined. Almost a threefold increase in surface/volume ratio did not alter the order of the reaction rate or the formaldehyde maximum, though it slightly increased the hydrogen peroxide maximum. Packing inhibited the hydrogen peroxide formation. Experiments were also made in vessels coated with lead monoxide, boric oxide and silver and in a vessel of pure gold. Lead monoxide eliminated the peroxide and greatly diminished the reaction. Boric acid behaved rather similarly to a* Pyrex *surface treated with hydrogen fluoride. The gold surface prevented reaction, even at 500° C and 600 mm initial pressure. The effects of diluents such as nitrogen, argon and helium were investigated. The reaction rate and the percentage of formaldehyde increased slightly with increase in percentage of diluent. Water was found to have a slight promoting effect which was rather greater than that of carbon dioxide. The effect was relatively greater in a potassium chloride coated vessel, indicating that the diluent prevented access to the destructive surface. These and other results are discussed in relation to work on methane oxidation by Norrish, Hoare and Walsh, and others. It is concluded that other intermediates besides formaldehyde are controlling the rate and, as in the hydrogen-oxygen reaction, the radical HO_2 plays an important part through the reaction $HO_2+CH_4 \rightarrow H_2O_2+CH_3$. Alkaline and lead monoxide surfaces are particularly active in destroying HO_2. As in the hydrogen-oxygen reaction, H_2O_2 can also lead to branching of a higher kinetic order than that introduced by OH radicals.*

THE profound influence of the nature and condition of the surface on the slow combustion of methane has been noted by all the earlier workers. R. G. W. NORRISH and S. G. FOORD[1] observed that the absolute values of the reaction velocity were susceptible to fortuitous changes in the surface condition of the reaction vessel. They confirmed the experience of other workers that the rate of reaction is considerably lowered by allowing the surface of the reaction vessel to be exposed to the air between experiments. Apart, however, from the recent work by D. E. HOARE[2], and by D. E. HOARE and A. D. WALSH[3], no systematic study has been made to elucidate the role of the nature and condition of the surface on the reaction. Using the

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same quartz vessel, Hoare followed the effect of various treatments of the surface on the rate of reaction. He observed a diminuition in the rate when the vessel was left for several days, whether it was evacuated or filled with air. He also found that the reaction rate dropped when the vessel was heated to 950° C, whether evacuated or filled with oxygen at 1 atm pressure. The vessel surface so deactivated could not be brought back to normal by keeping the vessel in contact with any of the products of reaction. However, the rate was found to recover its former value if a sufficient number of consecutive reactions took place in the vessel. Hoare further found that the passage of an electric discharge through hydrogen, water vapour, methane or oxygen in the vessel, prior to introduction of the methane–oxygen mixture, brought the value of the rate of reaction towards that obtained in an 'aged' vessel in which successive experiments had been carried out. Cleaning the vessel with hydrofluoric acid produced a similar effect. In Hoare's work, as in most of the earlier work, the effect of these various factors was studied by measurement of the pressure change. No attempt had been made to investigate the manner in which the chemistry of the reaction is affected by the various factors associated with the nature and condition of the surface.

Hoare and Walsh[3] have also examined the effect of these different surfaces on the oxidation kinetics. Vessels treated with hydrofluoric acid permit the occurrence of autocatalysis, and inert gases then have less catalytic influence than in vessels which are aged or treated otherwise. Furthermore, the activation energy and the reaction order was less in vessels treated with hydrofluoric acid. D. E. CHEANEY and A. D. WALSH[4] have been able to show that hydrofluoric acid treatment leaves a very thin film of silicic acid.

In the present work, a detailed study has been made of the influence exerted by the condition of the surface of *Pyrex* vessels upon the rate and nature of oxidation as measured by pressure change and by following the rate of formation of the intermediates, *viz.* formaldehyde and hydrogen peroxide. The experiments have been extended to vessels made of other materials.

EXPERIMENTAL

An account (with diagrams) of the apparatus and method used in these investigations was given in the paper on the slow oxidation of methane by A. C. EGERTON, G. J. MINKOFF and K. C. SALOOJA[5] in 1956 and it does not seem necessary to repeat the description. Formaldehyde was estimated colorimetrically with the chromotropic acid reagent using a spectrophotometer; hydrogen peroxide and other peroxides were estimated by the methods developed by the authors and others and described elsewhere[5].

The results of experiments which bear particularly on the effects which surfaces have on the course of oxidation of methane will be described in some detail under special headings.

EFFECT OF THE CONDITION OF SURFACE ON THE REACTION

Pyrex vessels—At an early stage in this investigation, as has been mentioned in the previous paper[5], it was observed that with *Pyrex* vessels maximum reaction rates were obtained with vessels which had been cleaned with

hydrofluoric acid before use. Furthermore, when using such vessels, no difficulty was experienced in obtaining concordant and reproducible results. Hoare also found that a silica surface which had been 'deactivated' by heating to 950°C could be restored to normal activity by treatment with hydrofluoric acid.

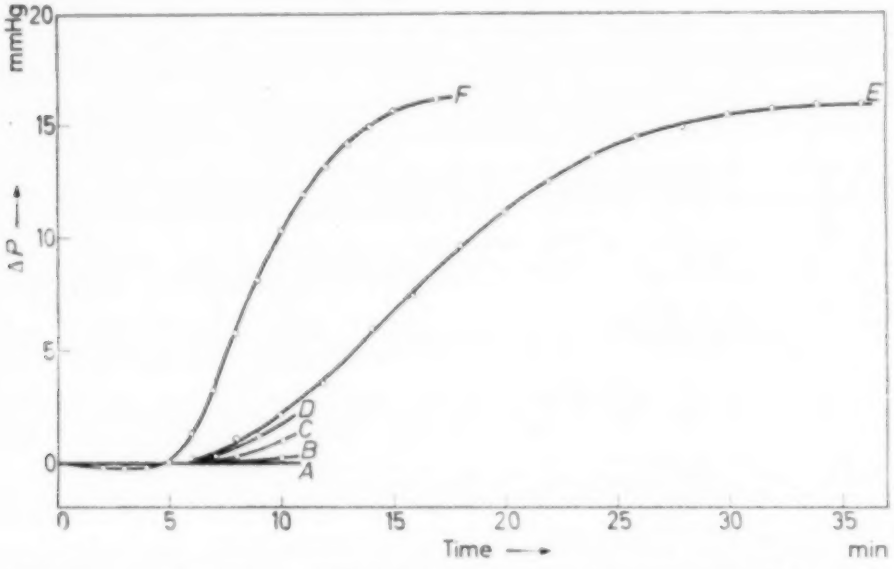

Figure 1. Reaction of CH_4+2O_2 *in a* Pyrex *vessel at 460°C and 350 mm* Hg. A, B, C, D *and* E *in an untreated vessel (successive runs); F in a vessel treated with hydrofluoric acid*

Reactions were carried out using (CH_4+2O_2) mixtures at 460°C and 350 mm Hg pressure in a *Pyrex* reaction vessel with a 6 cm internal diameter and surface-to-volume ratio of 1·0 cm^{-1}. It was found that, in a vessel cleaned with hydrofluoric acid, the pressure starts rising after an induction period of about 5 min and is well past its maximum rate of increase after 10 min with a pressure rise of over 10 mm Hg. While on the other hand, in the untreated vessel, there was no change in pressure at all for such lengths of time in the first run, as shown in *Figure 1*; in the second run there

Table 1. The amount of formaldehyde and hydrogen peroxide present at the end of 10 min in the course of the reaction of CH_4+2O_2, *at 460°C and 350 mm* Hg *in an untreated* Pyrex *vessel,* $S/V=1·0\,cm^{-1}$

Run	*Formaldehyde present at the end of the run* μg	*Hydrogen peroxide present at the end of the run* μg
1	22·5	4·7
2	47·2	7·3
3	61·0	12·2
4	70·8	14·0
5	77·3	16·3
6	83·0	19·3
7	81·7	20·7
8	85·1	21·0
9	83·4	21·8

was a slight rise, and in the third and subsequent runs the rate of pressure rise went on increasing till it seemed to have reached a steady, reproducible stage after the fifth run. In all these runs the reaction was stopped after 10 min and the condensable products were examined for their formaldehyde and hydrogen peroxide contents. The results of these analyses are given in *Table 1*.

After a number of runs, when the state of the surface of the vessel was such that reasonably reproducible results were being obtained, the reaction was carried out at various pressures ranging from 250 to 450 mm Hg and at temperatures from 460° to 500° C to evaluate the order of reaction and the activation energy with the surface in this condition. Some of the pressure–time data are plotted in *Figure 2*. From these results the order of

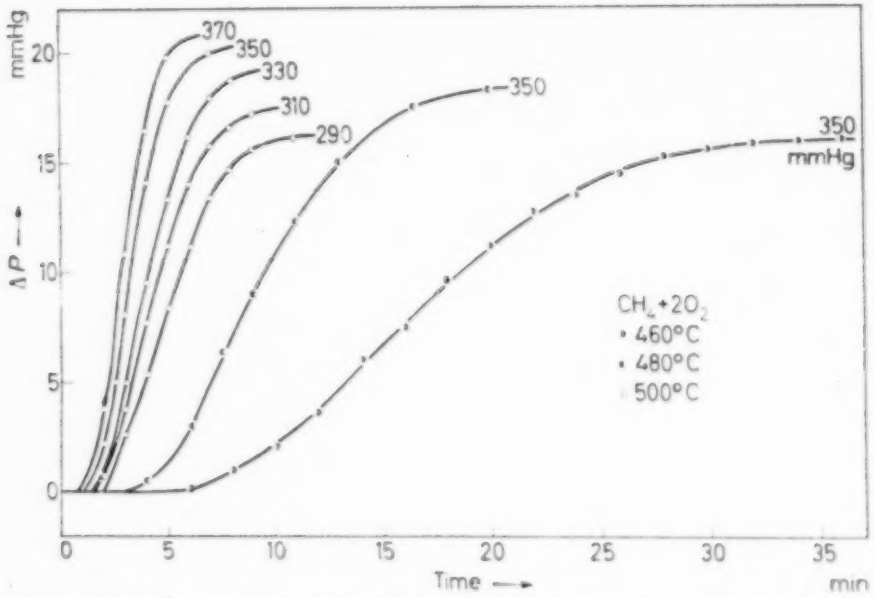

Figure 2. Effect of temperature and pressure on the reaction of $CH_4 + 2O_2$ *in an untreated* Pyrex *vessel* ($S/V = 1{\cdot}0\ cm^{-1}$). *The figure against each curve is pressure (mm* Hg)

reaction was found to be 3·9 at 500° C and the activation energy, 60·8 kcal at 350 mm Hg pressure (agreeing with Norrish and Foord's value of 4·0 for the order and with R. Fort and C. N. Hinshelwood's[6] of 61·5 kcal for the activation energy).

The vessel used was then treated with dilute hydrofluoric acid and thoroughly washed with distilled water at room temperature till completely free of acid. The rate of reaction now, as previously with vessels treated with hydrofluoric acid, was much faster than in the untreated vessel (*Figure 1*). It was reproducible after the first or, at the most, the second run. The rates of formation of formaldehyde and of hydrogen peroxide in the course of the reaction were determined and the results included in *Figure 3*. Associated with the much lower rate of reaction in the untreated vessel, there was a very much smaller formation of hydrogen peroxide (see *Table 1*).

At about the same stage of pressure rise as that corresponding to the fifth run, there would have been about 150 μg of hydrogen peroxide formed in the vessel treated with hydrofluoric acid. The amount of formaldehyde formed was also less, but the rate of formation of hydrogen peroxide was affected to a much greater extent.

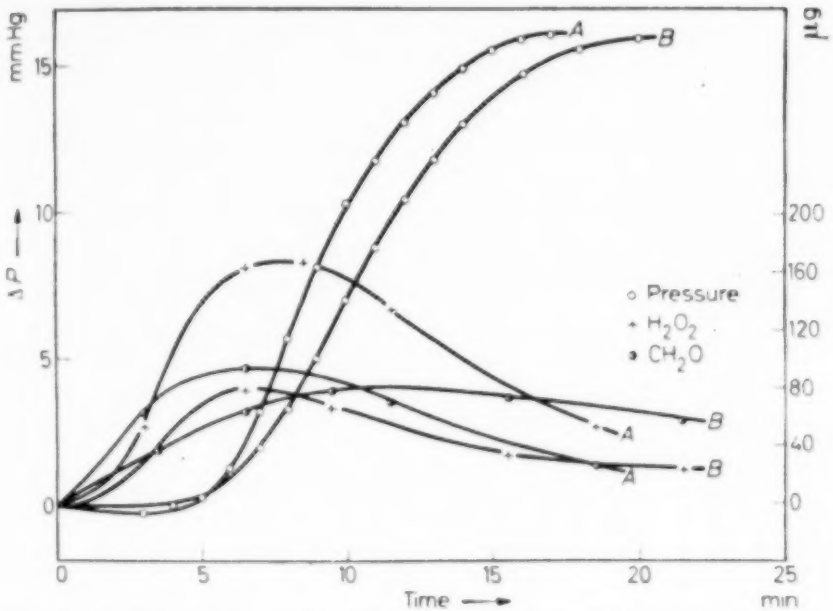

Figure 3. Rate of formation of formaldehyde and hydrogen peroxide in a Pyrex *vessel treated with hydrofluoric acid.* A *Freshly treated vessel;* B *After 20 weeks' standing*

In the vessel treated with hydrofluoric acid, the order of reaction and the activation energy were found, from the data shown in *Figure 4*, to be 2·3

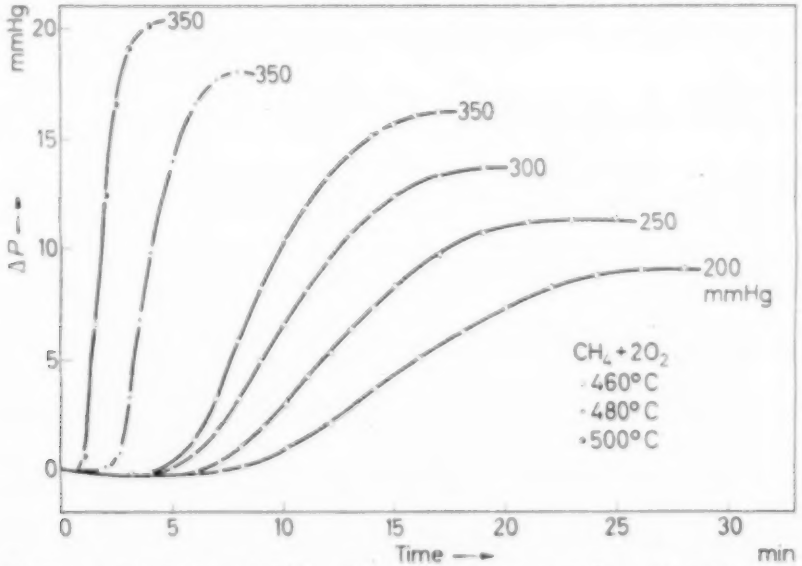

Figure 4. Reaction of CH_4+2O_2 *in a* Pyrex *vessel* ($S/V=1{\cdot}0\,cm^{-1}$) *treated with hydrofluoric acid*

and 39·3 kcal respectively, which agree well with the values obtained in larger vessels treated with hydrofluoric acid, having a surface-to-volume ratio of $0{\cdot}8\,cm^{-1}$.

Thus, comparisons of the reaction in untreated and in treated *Pyrex* vessels showed that, in the untreated vessel, the order of reaction and the overall activation energy of the reaction were much higher, while the formation of formaldehyde was reduced and the formation of detectable hydrogen peroxide strongly inhibited.

The vessel treated with hydrofluoric acid, after a lapse of twenty weeks during which time it had been left unsealed, was again used in order to examine whether leaving the vessel idle for some length of time had any effect on the reaction. Without retreatment, the rate of reaction at various pressures and temperatures was then found to be lower. From the data in *Figure 5*, the value for the order of reaction was found to be 3·2 and that for the activation energy, 50·3 kcal. This showed a considerable increase over the respective values of 2·3 and 39·3 kcal obtained for the reaction under the same conditions in the vessel after it had been freshly treated with hydrofluoric acid, but was still considerably lower than those obtained with an untreated reaction vessel.

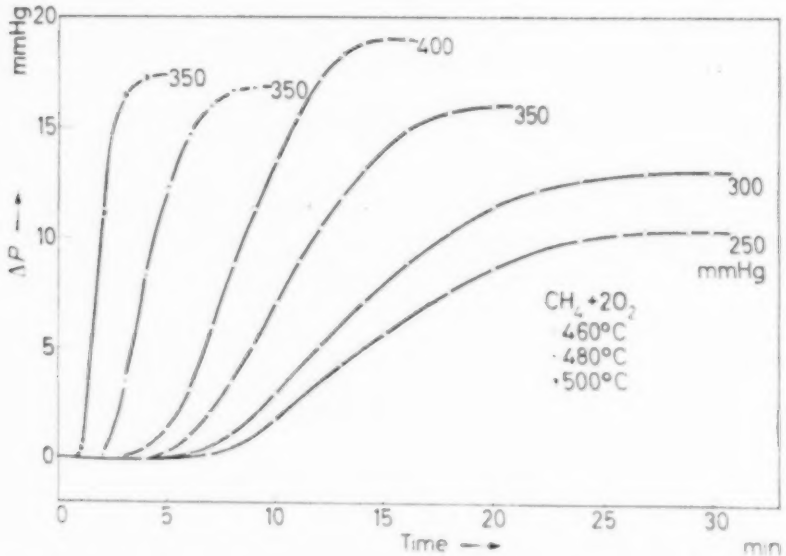

Figure 5. Reaction of CH_4+2O_2 *in a* Pyrex *vessel* ($S/V=1{\cdot}0\,cm^{-1}$) *treated with hydrofluoric acid and left standing for 20 weeks*

The rate of formation of formaldehyde and hydrogen peroxide was determined during the course of the reaction at 460 C and 350 mm Hg pressure. The results have been plotted in *Figure 3*, together with those obtained with a freshly treated vessel. As observed in the reaction in an untreated vessel, the most striking point was again the effect on the formation of hydrogen peroxide. In the vessel freshly treated with hydrofluoric acid, the rate of reaction was fastest, and so was the rate of formation

of formaldehyde and hydrogen peroxide. In the treated vessel which had been left unused for a considerable length of time, changes in the nature of the surface occurred which retarded reaction and inhibited formation of hydrogen peroxide. In the untreated *Pyrex* vessel, the rate of reaction and the amount of hydrogen peroxide present in the products were still lower. Thus the values obtained for the reaction velocity, activation energy and order were related to the effect of the surface on the formation or destruction of hydrogen peroxide.

Soda glass vessels—Similar experiments were undertaken in a soda glass vessel of the same size as the *Pyrex* vessel used above. A ($CH_4 + 2O_2$) mixture was introduced into the untreated soda glass vessel at 460 °C and 350 mm Hg pressure. There was no rise in pressure within half an hour, even after carrying out twelve successive runs. There was also no pressure change after half an hour with an initial reactant pressure of 450 mm Hg. Analysis of the products after the runs at 350 mm Hg showed that there was no hydrogen peroxide formed and that formaldehyde was present only in very small amounts—about 8 μg at the end of 10 min and about 25 μg after half an hour.

The soda glass reaction vessel was then cleaned with hydrofluoric acid using the same technique as for the *Pyrex* vessels. Again, even after carrying out a number of successive runs, there was no rise in pressure for

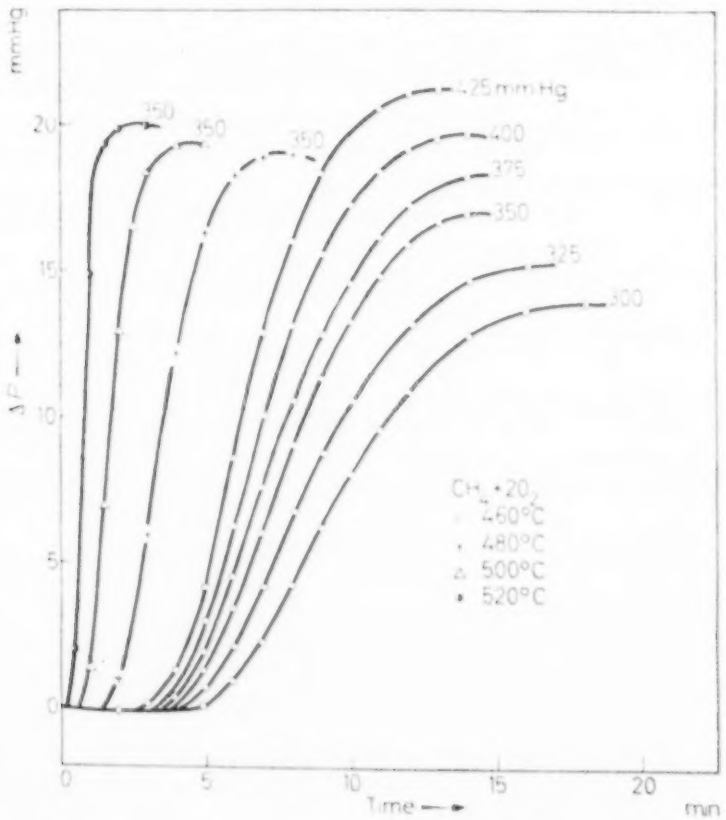

Figure 6. Reaction of $CH_4 + 2O_2$ in an untreated silica vessel ($S/V = 1.0\,cm^{-1}$) at different temperatures and pressures

half an hour. At the end of these runs, it was found that there was hardly any peroxide present and that the amount of formaldehyde formed (10 μg at the end of 10 min and 31 μg after $\frac{1}{2}$ h) was not much different from that formed in the untreated soda glass vessel. There was hardly any rise in pressure when the reaction mixture was introduced into the vessel at 450 mm Hg. After half an hour, products on analysis showed the presence of 51 μg of formaldehyde but again no hydrogen peroxide could be detected.

Thus in soda glass vessels the reaction was very strongly inhibited, and even treatment with hydrofluoric acid had hardly any effect.

Silica vessels—In silica vessels, the results obtained differed only slightly from those with *Pyrex* glass vessels, but were quite different from those with soda glass. In the untreated silica vessels (surface: volume = 1·0 cm^{-1}), there was no inhibition of the reaction whatsoever in the first few runs, and a fast reproducible rate of reaction set in immediately. The data on the course of reaction at different pressures and temperatures are plotted in *Figure 6*. A value of 2·2 for the order of the reaction was found, which is very

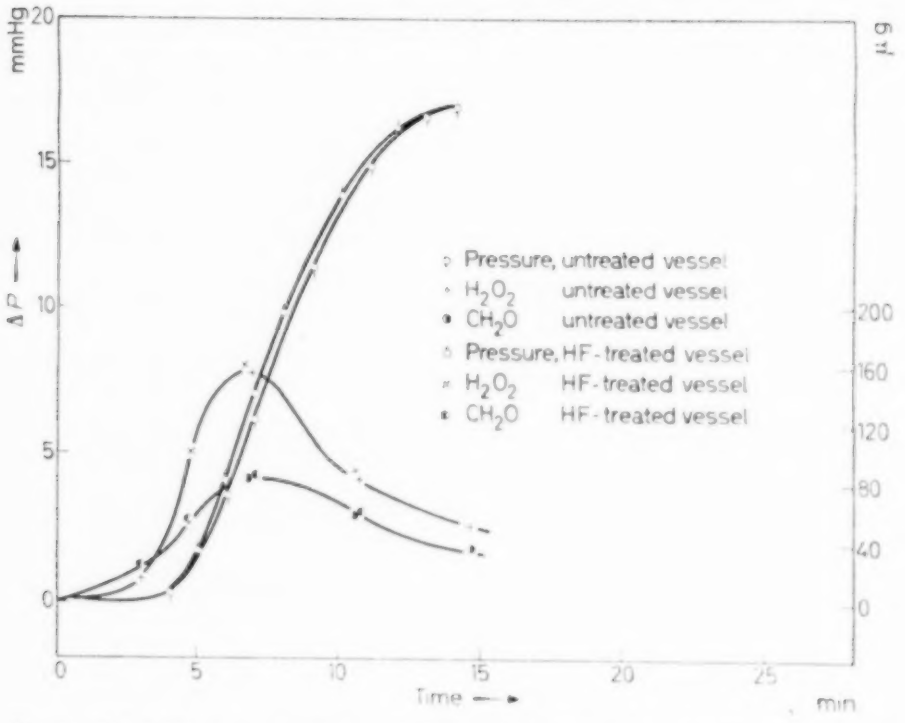

Figure 7. Rate of formation of formaldehyde and hydrogen peroxide during the reaction $CH_4 + 2O_2$ *at 460° C and 350 mm* Hg *in a silica vessel before and after treatment with hydrofluoric acid*

close to that obtained with *Pyrex* vessels freshly treated with hydrofluoric acid. The value for the activation energy was however slightly higher, *viz.* 45 kcal. The rate of formation of formaldehyde and hydrogen peroxide using the mixture ($CH_4 + 2O_2$) at 460° C and 350 mm Hg was determined; the results are plotted in *Figure 7*. The amounts of formaldehyde and

hydrogen peroxide formed at different stages were similar to those obtained in *Pyrex* vessels which had been freshly treated with hydrofluoric acid.

No changes in the results were found when the silica vessel was treated with hydrofluoric acid and the above experiments repeated. The pressure–time data on the course of the reaction are shown in *Figure 8*.

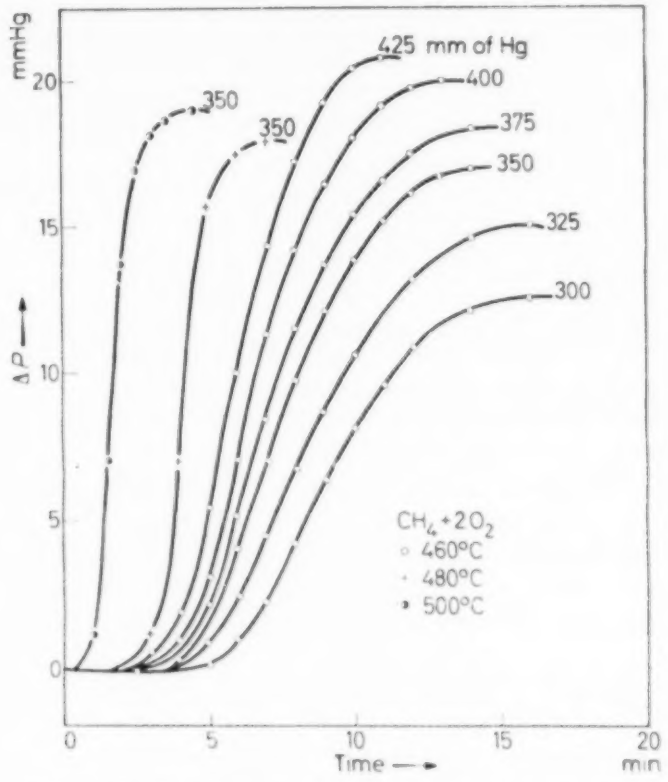

Figure 8. Reaction of CH_4+2O_2 *in a silica vessel* ($S/V=1{\cdot}0\,cm^{-1}$) *treated with hydrofluoric acid, at different temperatures and pressures*

THE EFFECT OF VARYING THE SURFACE-TO-VOLUME RATIO OF THE REACTION VESSEL

It has been observed by most of the earlier investigators that there is a diminution in the reaction rate in vessels of smaller diameter and that no reaction takes place in packed vessels. W. A. BONE and J. B. GARDNER[7] found that the percentage of formaldehyde formed in the system at the end of the induction period, as well as the rate of oxidation during the subsequent reaction period, varied inversely with the surface-to-volume ratio in silica vessels when the surface-to-volume ratio was changed by the introduction or withdrawal of cylindrical silica rods. Norrish and Foord found that the order of reaction increased in *Pyrex* vessels as the surface-to-volume ratio was increased, with decreasing diameter of the vessels. However, in the light of the observations on the manner in which the surface of the reaction vessel affected so markedly the course of the reaction, it was considered necessary to re-examine the effects on the reaction of varying the surface-to-volume ratio of the vessel.

In the present work, the reaction was studied in *Pyrex* vessels of different sizes, all cleaned beforehand with hydrofluoric acid in the manner described. The values for the order of reaction and the activation energies obtained in vessels of various sizes are given in *Table 2*. These show practically no change in the value of either the order of reaction or the activation energy,

Table 2. The order of reaction and the activation energy in Pyrex *vessels of different sizes treated with hydrofluoric acid*

Surface: volume ratio cm^{-1}	*Order of reaction*	*Activation energy kcal*
0·8	2·4	39·1
1·0	2·3	41·7
1·2	2·2	43·4
1·5	2·2	40·0
2·0	2·4	42·2

as the surface-to-volume ratio is varied. This is contrary to the observation of Norrish and Foord, that the order of reaction increased with increasing surface-to-volume ratio of the vessel. The results obtained did not indicate that changing the surface-to-volume ratio *within* the above range involved any change in the reaction mechanism. When the rates are corrected for the variation in sharing ratio with the Foord gauge, it is found that the maximum rate of pressure change only increases very slightly with increasing vessel diameter. Both formaldehyde and hydrogen peroxide were formed in the smaller vessels as well as in the bigger vessels. The peak concentrations of formaldehyde and hydrogen peroxide present during the course of the reaction at 460° C and 350 mm Hg initial pressure in different vessels are given in *Table 3*, as percentages of the total products. These results show that, whereas the maximum concentration of formaldehyde formed in vessels of different sizes did not change much, that of hydrogen peroxide

Table 3. Approximate maximum concentration of formaldehyde and hydrogen peroxide formed in vessels of different sizes using $(CH_4 + 2O_2)$ *at 460° C and 350 mm* Hg

Surface: volume ratio cm^{-1}	*Formaldehyde (maximum)* %	*Hydrogen peroxide (maximum)* %
0·8	0·33	0·53
1·0	0·32	0·57
1·2	0·31	0·58
1·5	0·31	0·61
2·0	0·30	0·65

increased appreciably with increasing surface-to-volume ratio. These observations suggest that the formation of hydrogen peroxide occurs to some extent on the surface of the reaction vessel.

Reaction in packed vessels—A *Pyrex* vessel, 7 cm in diameter, was fully packed with 250 cylindrical rings of *Pyrex* glass, external diameter 0·75 cm, internal diameter 0·55 cm, and length 1 cm, after both the vessel and the

rings had been treated with hydrofluoric acid. The surface-to-volume ratio of the packed vessel was calculated to be $8{\cdot}8\,cm^{-1}$. When a $(2CH_4+O_2)$ mixture at 350 mm Hg pressure was introduced into the vessel at 460°C, there was no rise in pressure for as long as 1 h, whereas, in the unpacked

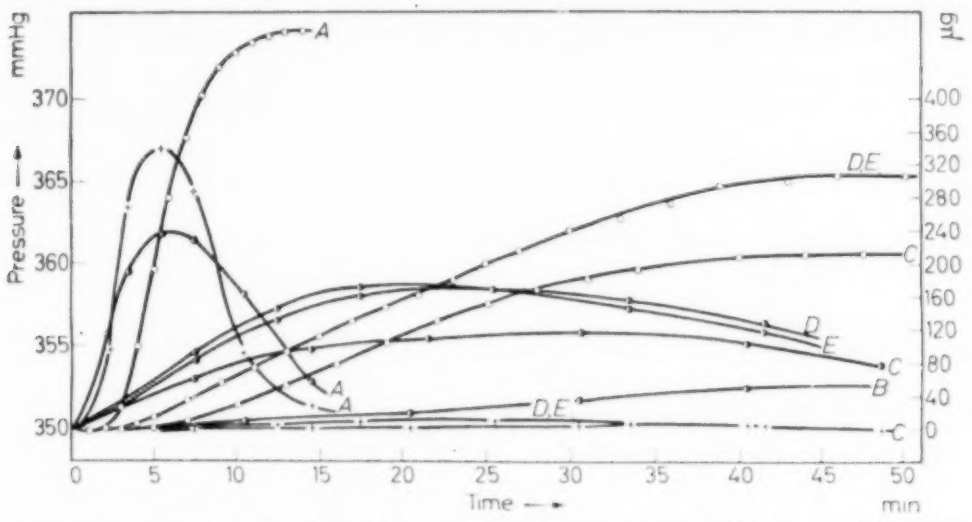

Figure 9. Reaction of $2CH_4+O_2$ *in packed vessels at 460°C and 350 mm* Hg
A *unpacked vessel treated with hydrofluoric acid;* B *packed vessel* $(S/V=8{\cdot}8\,cm^{-1})$;
C *packed vessel* $(S/V=4{\cdot}8\,cm^{-1})$; D *after unpacking the vessel with* $S/V=8{\cdot}8\,cm^{-1}$; E *after unpacking the vessel with* $S/V=4{\cdot}8\,cm^{-1}$
○ *pressure;* + H_2O_2; ◑ HCHO

vessel treated with hydrofluoric acid, as shown in *Figure 9*, the induction period was over in 2 min, the maximum pressure rise occurred in the fifth minute and the reaction was over in 13 min with a total pressure rise of about 24 mm Hg. The reaction mixture was left in the packed vessel for various lengths of time up to an hour and then chilled in the trap cooled in liquid air for examination of any intermediates formed. It was found that, while small amounts of formaldehyde were formed, which increased with the length of time the reactants were left in the vessel, no hydrogen peroxide whatsoever was detectable. From the results of experiments in the previous section, it might be expected that there would be more chance of formation of hydrogen peroxide as the surface-to-volume ratio in the packed vessel was increased. On the other hand, the fact that the reaction hardly occurred at all in the packed vessel and that the formation of hydrogen peroxide was strongly inhibited, seems to parallel the observations made in vessels with chain-breaking surfaces.

The vessel was then unpacked and resealed on to the apparatus. On introduction of the $(2CH_4+O_2)$ mixture to attain a pressure of 350 mm Hg in the vessel at 460°C, the rate of reaction was far slower than it was when the vessel had been freshly treated with hydrofluoric acid. It was also found that, while the concentration of formaldehyde did not fall far short of that in vessels freshly treated with hydrofluoric acid, that of hydrogen peroxide was being strongly inhibited, leaving little doubt that the surface had changed. As a further check on this point, the reaction vessel was

treated with hydrofluoric acid and the reaction carried out again under the same conditions. This time, the rate of reaction reverted to its original high value and, furthermore, the concentrations of both formaldehyde and hydrogen peroxide were the same as in the treated vessels without packing.

This series of experiments was repeated in the same *Pyrex* vessel which had been freshly treated with hydrofluoric acid. This time the vessel was packed with larger cylindrical rings of *Pyrex*—external diameter 1·16 cm, internal diameter 0·95 cm, and length 1·6 cm—such that the surface-to-volume ratio was 4·8 cm^{-1} instead of 8·8 cm^{-1} as in the previous instance. As shown in *Figure 9*, the reaction, though quite slow, did take place. Again it was mainly the formation of hydrogen peroxide which was being strongly affected. After unpacking the vessel, the rate of reaction, as well as the rate of formation of intermediates, remained slow, and, as shown in *Figure 9*, were of the same order of magnitude as those obtained in the previous experiment with the smaller rings. When the vessel was again treated with hydrofluoric acid, it gave rise to normal rates of reaction and of formation of intermediates.

These experiments suggest that heating a reaction vessel containing pieces of glass brings about some change in the nature of the surface, possibly the migration of alkali ions from the body of the glass through the sharply cut edges of the cylindrical rings on the surface of the vessel. This suggestion seems to be supported by experiments in which soda glass cylindrical rings were packed into the same *Pyrex* vessel as used above, after the vessel and the rings had been treated with hydrofluoric acid. The reaction was completely inhibited in the packed vessel, with surface-to-volume ratio of 5·7 cm^{-1}, and on unpacking the vessel there was again no rise in pressure for an hour. No trace of hydrogen peroxide could be detected in the intermediates examined at various stages of the reaction in the unpacked vessel and formaldehyde was present only in small amounts. On retreatment with hydrofluoric acid, however, the normal rates of reaction and of formation of hydrogen peroxide and formaldehyde were again obtained. However, when a crack in such a vessel was repaired by normal glass-blowing methods, and a run was carried out without again cleaning the surface, the very slow rate was again obtained.

Summarizing the results, the experiments show: (*a*) that, in *Pyrex* vessels of surface-to-volume ratio between 0·8 and 2·0 cm^{-1} whose surfaces were cleaned with hydrofluoric acid, increase in the ratio has little effect on the rate, activation energy or reaction order; (*b*) that increase of surface tends to increase slightly the amount of hydrogen peroxide isolated; (*c*) that any treatment involving glass-blowing of the vessel, including the introduction or the removal of *Pyrex* rings, decreases the rate markedly, reduces the amount of formaldehyde isolated and inhibits the formation of hydrogen peroxide. The inhibition can be elimited by treatment with hydrofluoric acid.

THE REACTION IN COATED VESSELS AND IN METAL VESSELS

Comparatively little work has been done on the slow combustion of methane in coated vessels. It was known that lead oxides caused inhibition of the oxidation of methane and other hydrocarbons. D. E. Hoare and A. D.

WALSH[8] have recently studied the marked diminution of the maximum rate of pressure rise on the oxidation of methane that is caused by a lead monoxide coating, though they found that it had little effect on the induction period. Hoare[2] also examined the effect of coating the reaction vessel with potassium chloride and found that the reaction, though slower than in uncoated vessels, is not as slow as with lead monoxide coated vessels. However, in this work, as in their other work on the oxidation of methane, Hoare and Walsh did not examine the products of reaction.

In the present investigations, the reaction has been studied in vessels coated with potassium chloride, potassium hydroxide, boric oxide and lead monoxide, in silvered vessels and in a vessel made of pure gold. The products of each reaction, particularly the formation of formaldehyde and hydrogen peroxide, as well as the rate of pressure rise, have been examined in each case.

The reaction in vessels coated with potassium chloride—Potassium chloride was selected as one of the substances with which to coat the vessels since a considerable amount of work has already been done in such vessels on the hydrogen–oxygen reaction and it has been shown that potassium chloride has a high efficiency in destroying certain types of chain carrier.

A *Pyrex* spherical bulb—7 cm in diameter, surface-to-volume ratio 0·86 cm^{-1}—fitted with two connecting tubes, a capillary and a wide-bore tube, was treated with hydrofluoric acid and washed thoroughly with distilled water till free of acid. The wide-bore connecting tube was sealed off near the end where it joined the bulb, while the capillary connecting tube linked the vessel to the rest of the apparatus through a ground glass

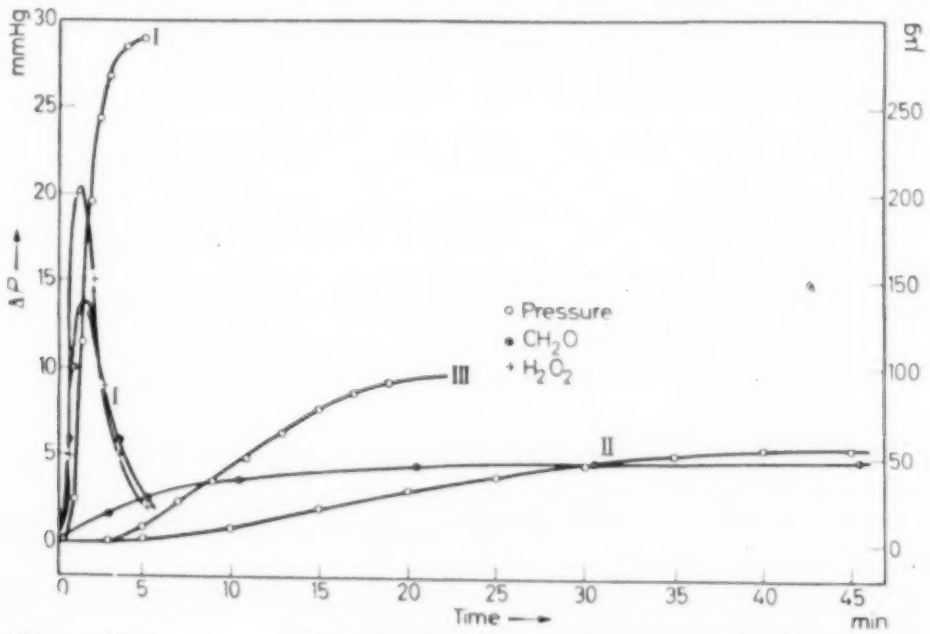

Figure 10. Reaction of $CH_4 + O_2$ *at 500°C in a vessel coated with potassium chloride.* I *uncoated vessel treated with hydrofluoric acid, 350 mm* Hg; II *vessel coated with potassium chloride, 350 mm* Hg; III *vessel coated with potassium chloride, 500 mm* Hg

joint. The rate of pressure rise and the rate of formation of both formaldehyde and hydrogen peroxide were determined in the *Pyrex* vessel treated with hydrofluoric acid using a ($CH_4 + O_2$) mixture at 500°C and 350 mm Hg (see *Figure 10*). The wide-bore connecting tube was then re-joined to the bulb and the vessel rinsed with an aqueous solution of potassium chloride (*AnalaR*). It was then sealed off as before, and the vessel connected to the apparatus. Using the ($CH_4 + O_2$) mixture, the reaction was examined in the same vessel coated with potassium chloride, again at 500°C and 350 mm Hg pressure. As shown in *Figure 10*, the rate of pressure rise was very slow. Whereas, in the vessel treated with hydrofluoric acid, the reaction passed through the maximum velocity during the second minute after an induction period of only 30 sec and was complete in 5 min with a total pressure rise of about 29 mm Hg, after coating the same vessel with potassium chloride, the pressure had risen very slowly by only 5·7 mm Hg at the end of 45 min. Analysis of the products showed that formaldehyde was formed in the course of the reaction and its rate of formation has been plotted in *Figure 10*. However, no hydrogen peroxide whatever was detected. When the pressure of the reactants was raised to 500 mm Hg, the rate of reaction became much higher. Considerably larger amounts of formaldehyde were formed but again hardly any hydrogen peroxide could be detected in the products.

The reaction in vessels coated with potassium hydroxide—A coating of potassium hydroxide was tried next. As before, the rates of pressure rise and of formation of formaldehyde and hydrogen peroxide were established in a vessel treated with hydrofluoric acid. The vessel was then coated with potassium hydroxide (*AnalaR*) and, on carrying out the reaction, there was no rise in pressure at either 350 or 500 mm Hg. There was no hydrogen peroxide formed and only traces of formaldehyde (less than 5 μg) could be detected in the reaction mixture after various periods of time up to 1 h.

Thus the fact that the reaction was very slow in the vessel coated with potassium chloride and was inhibited even more in that coated with potassium hydroxide, leads to the same conclusion as that reached in the study of the hydrogen–oxygen reaction, *i.e.* that such coatings have a high efficiency for destroying chain-carrying particles[16]. Coupled with this observation, the fact that no hydrogen peroxide was formed in the coated vessels further helped to identify the chain-carrying particles responsible for the formation of hydrogen peroxide with those chiefly responsible for the attack on methane.

The reaction in vessels coated with boric oxide—The reaction was investigated in vessels coated with boric oxide because these are usually regarded as providing a surface condition which prevents decomposition of hydrogen peroxide.

The reaction was first carried out in a *Pyrex* vessel treated with hydrofluoric acid, 7 cm in diameter and with a surface-to-volume ratio of 0·86 cm^{-1}. The rates of pressure rise, as well as the rates of formation of formaldehyde and hydrogen peroxide, were determined using a ($CH_4 + O_2$) mixture at 500°C and 350 mm Hg (*Figure 11*) and were found to compare

well with those obtained in previous experiments carried out under similar conditions. The reaction vessel was then treated with a saturated solution of boric acid (*AnalaR*) in distilled water so as to deposit a thick coating of boric oxide on drying. As shown in *Figure 11*, the rate of pressure rise was rather slow at first and, after a few minutes, began to fall, indicating that in all probability the thick coating of boric oxide was absorbing some

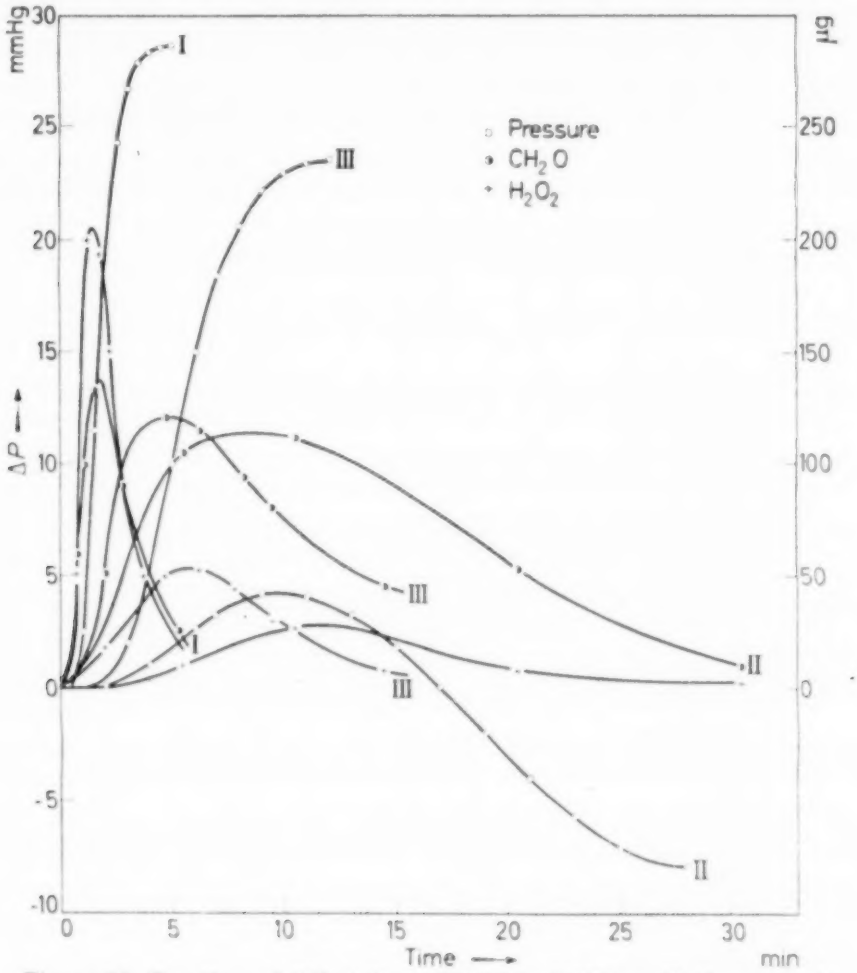

Figure 11. Reaction of $CH_4 + O_2$ *at 500° C and 350 mm* Hg *in a vessel coated with boric oxide.* I *uncoated vessel treated with hydrofluoric acid;* II *vessel with thick coating of boric oxide;* III *vessel with thin coating of boric oxide*

products of oxidation such as water. The peak concentration of formaldehyde formed in the course of the reaction was not much affected, but the peak concentration of hydrogen peroxide was lower. It was thought that perhaps the roughness of the thick deposit prevented a high yield of hydrogen peroxide. The formation of hydrogen peroxide in the vessel coated with boric oxide was, however, by no means completely inhibited.

The reaction vessel was then repeatedly washed out with cold water and sealed on to the apparatus with a much thinner layer of boric acid left on it. As shown in *Figure 11*, the rate of pressure rise was now very much

higher and the maximum concentration of hydrogen peroxide, though not as high as that in the uncoated vessel treated with hydrofluoric acid, was higher than that obtained in the thickly coated vessel.

The reaction in vessels coated with lead oxide—As mentioned earlier, Hoare and Walsh recently described experiments in which they obtained a marked diminution in the maximum rate of pressure rise in vessels coated with lead monoxide at 500°C using a ($2CH_4 + O_2$) mixture at 500 mm Hg pressure, although they found the induction period to be unaffected, relative to that obtained on aged or heat-treated surfaces.

In the present work, a spherical bulb of *Pyrex* glass (internal diameter 7 cm) was first treated with hydrofluoric acid and the rates of pressure rise and of formation of intermediates were confirmed to be the same as obtained in other experiments carried out under similar conditions. A very small amount of lead monoxide powder was introduced into the vessel and the vessel heated to about 580°C under vacuum, when a thin film of lead monoxide with a bluish irridescence was uniformly deposited on the glass. At 500°C, using a ($CH_4 + O_2$) mixture at 350 mm Hg pressure, there was no change in pressure whatsoever for an hour. Neither hydrogen peroxide nor formaldehyde could be detected in the reaction mixture during this run. On raising the pressure of the reaction mixture to 500 mm Hg, there was again hardly any rise in pressure, though small amounts of formaldehyde (about 10 μg) could be detected after half an hour.

Similar experiments in the vessel coated with lead monoxide, using a methane rich mixture ($2CH_4 + O_2$), again showed that at 350 mm Hg there was no rise in pressure and no formation of either hydrogen peroxide or formaldehyde. On carrying out the reaction at 500 mm Hg pressure, a slight rise in pressure was noticeable after half an hour and the pressure began to rise very slowly until, at the end of 1 h, it had risen by only about 4 mm Hg. There was no hydrogen peroxide formed in the course of this run, but formaldehyde was present in small amounts, about 20 μg at the end of $\frac{1}{2}$ h and 41 μg after 1 h.

Another *Pyrex* vessel was coated with a much thinner film of lead monoxide from a side tube connected to the vessel when the whole system was under vacuum. In this instance no bluish irridescence was visible on the surface. On carrying out the reaction with an equimolecular mixture of methane and oxygen at 500°C and 450 mm Hg pressure, reaction occurred with appreciable rise in pressure. However, the rate of pressure rise was less than that in vessels coated with potassium chloride. The induction period was also longer. There was no trace of hydrogen peroxide in the products of reaction either in the vessel coated with lead monoxide or in that coated with potassium chloride. In both, the rise in pressure was accompanied by the formation of easily detectable amounts of formaldehyde.

Thus, a thin lead monoxide coating strongly inhibits the slow oxidation of methane and markedly affects the induction period. Compared with a potassium chloride coating, the reaction is more strongly inhibited.

The reaction in silvered vessels—A *Pyrex* vessel treated with hydrofluoric acid, in which the rate of reaction had previously been established, was

silvered by the Rochelle salt method. The silvered surface was washed very thoroughly with water till free of salts. At a temperature of 500° C, using a $(CH_4 + O_2)$ mixture at 350 mm Hg pressure, there was no rise in pressure and no formaldehyde or hydrogen peroxide was formed. At 500 mm Hg pressure there was a slight drop in pressure, most probably due to absorption of some oxygen by silver. No hydrogen peroxide could be detected at the end of half an hour, but a trace of formaldehyde (about 10 μg) was found in the products.

The reaction in a gold vessel—Hydrogen peroxide is very easily destroyed by a silver surface and rather less easily by a gold surface, so the reaction was next studied in a vessel 5 cm in diameter made of pure gold (surface-to-volume ratio 1·2 cm^{-1}). Using a $(CH_4 + 2O_2)$ mixture at 500° C, there was no rise in pressure even at a pressure of 600 mm Hg. Neither hydrogen peroxide nor formaldehyde could be detected at any stage of the reaction up to half an hour.

THE EFFECT OF ADDITIVES

The effect of the addition of inert gases, products of combustion and some sensitizers and inhibitors on the oxidation of methane has been examined by various workers in the past. Rather conflicting conclusions have been reached regarding the effect of the addition of water. W. A. Bone and R. E. Allum[9], and more recently M. Vanpée[10], showed that the addition of water vapour in small amounts, up to 2 per cent, caused an acceleration of the reaction and shortening of the induction period. Norrish and Foord[1], however, found that the addition of water vapour had no such catalytic effect on the reaction, apart from the increase in the rate of reaction similar to that which they found was brought about by the addition of an inert gas.

In the present work, the effect of the addition of inert gases and some products of reaction on the rate of oxidation of methane and the rate of formation of intermediates was further examined.

The effect of the addition of nitrogen—The effect of the addition of nitrogen, and also of other additives, was studied in a *Pyrex* vessel treated with hydrofluoric acid, 7 cm in diameter with surface-to-volume ratio of 0·86 cm^{-1}. The reaction was first carried out without any additive and the rates of pressure rise and of formation of formaldehyde and hydrogen peroxide determined. A quick method of conducting the experiment which gave good mixing consisted in introducing the inert gas or the reactants (preferably the former) first, and then evacuating the pipette space after closing the tap to the reaction vessel. The pipette space was then filled with reactants at a pressure higher by a predetermined amount than that inside the reaction vessel, such that on opening the tap the gases inside the reaction vessel would have the required mixture composition (see diagram of apparatus referred to on p. 26). The effect of adding various amounts of nitrogen to a $(CH_4 + 2O_2)$ mixture at 250 mm Hg pressure was determined and, similarly, the addition of nitrogen to the equimolecular mixture of methane and oxygen. The rate of reaction thus gradually increased with increasing pressure of nitrogen, as was first observed by Norrish and Foord. Using a $(CH_4 + O_2)$ mixture at 460° C, the rates of formation of hydrogen

peroxide and formaldehyde were measured at 250 mm Hg pressure, in the absence of nitrogen, and the experiment repeated after adding 250 mm Hg of nitrogen to the methane–oxygen mixture at the same pressure. The presence of nitrogen had only a slight effect on the concentration of the intermediates, that of formaldehyde seeming to be somewhat greater in the presence of nitrogen.

The effect of the addition of helium and argon—The addition of helium and argon was next investigated at 500°C in the *Pyrex* vessel treated with hydrofluoric acid, in the same manner as with nitrogen, keeping the partial pressure of the (CH_4+O_2) mixture in the reaction vessel constant at 200 mm Hg. The results showed a gradual increase in the rate of reaction with increasing addition of the inert gas. Care was taken to ensure the purity of the gases used. *Figure 12* illustrates one set of these measurements.

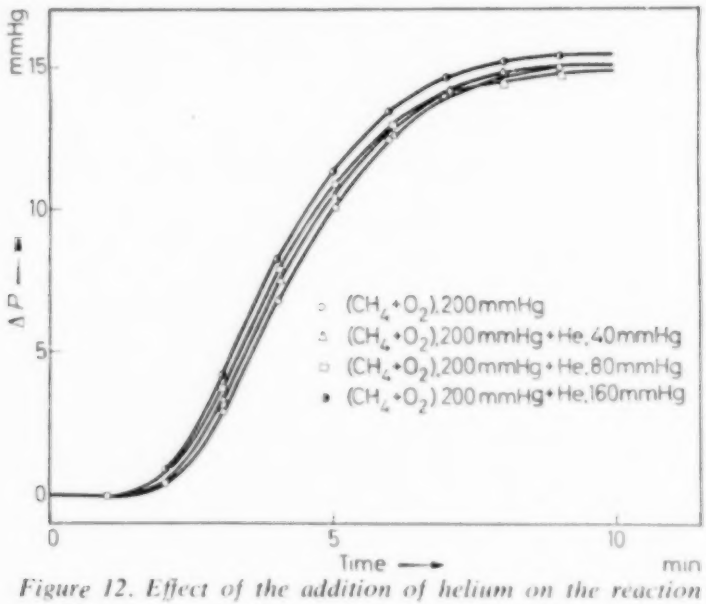

Figure 12. Effect of the addition of helium on the reaction of CH_4+O_2 at 500°C in a Pyrex *vessel ($S/V=0{\cdot}86\ cm^{-1}$) treated with hydrofluoric acid*

The effect of the addition of carbon dioxide—The results obtained with carbon dioxide under similar conditions also showed an increasing rate of reaction with increasing addition of carbon dioxide.

For a mixture containing carbon dioxide, and also for mixtures with helium and argon (80 mm Hg), the following amounts of intermediates were found to be present, on stopping the reaction after 3 min:

Additive	*Formaldehyde* μg	*Hydrogen peroxide* μg
Carbon dioxide	53	68
Argon	52	69
Helium	50	72

The effect of the addition of water—The mixture of ($CH_4 + O_2$) with water vapour was made in a reservoir kept at about 100°C to prevent the water vapour condensing. The results of the experiments in a *Pyrex* vessel treated with hydrofluoric acid, at 460°C and 250 mm Hg, are shown in *Figure 13*. They indicate a relatively greater increase in the rate of reaction caused by the addition of water as compared with the increases caused by addition of

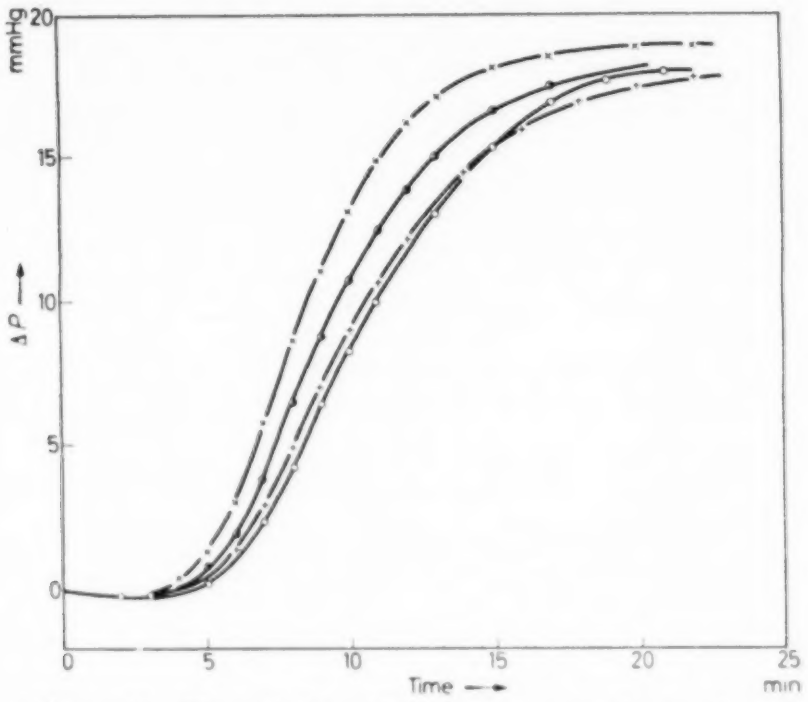

Figure 13. Effect of the addition of water on the reaction of $CH_4 + O_2$ *at 460°C in a* Pyrex *vessel* ($S/V = 0{\cdot}86\ cm^{-1}$) *treated with hydrofluoric acid. Partial pressure of reactants 250 mm* Hg. ○ *No additive;* + *5% additive;* ◑ *10 % additive;* × *20% additive*

carbon dioxide, nitrogen, argon and helium. The analysis of intermediates formed in the presence of water showed only a slight increase in the amounts of both formaldehyde and hydrogen peroxide formed. Thus with a mixture containing 5 per cent water, after $10\frac{1}{2}$ min, 102 μg of formaldehyde and 178·0 μg of hydrogen peroxide were found to be present, compared with 99·5 μg of formaldehyde and 174·7 μg of hydrogen peroxide present when there was no added water vapour.

In another experiment, water vapour was introduced separately into the reaction vessel, before the introduction of the reactants, to the same total pressure as with the premixed mixture. The results in *Figures 14* and *15* clearly show that the accelerating effect is then greater, thus indicating a greater activity of the surface when pretreated with water vapour.

In similar experiments using nitrogen, helium, argon and carbon dioxide as the additive, there was no change in the rate of reaction when the inert gas was introduced in the reaction vessel before or after the reactants.

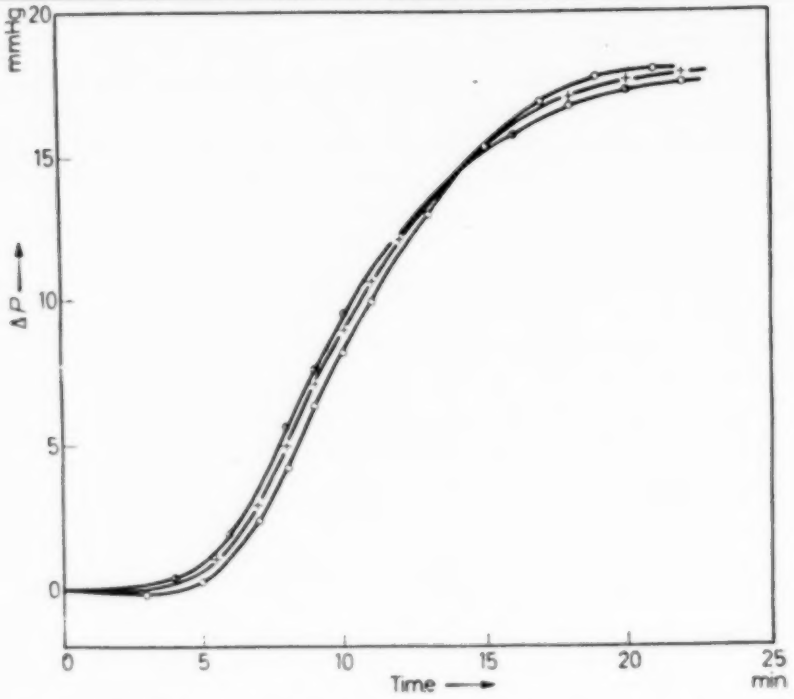

Figure 14. Effect of introducing 5 per cent water before the admission of reactants, conditions as for Figure 13. ○ *Reaction in the absence of water;* + *Water premixed with reactants;* ◑ *Water introduced before reactants*

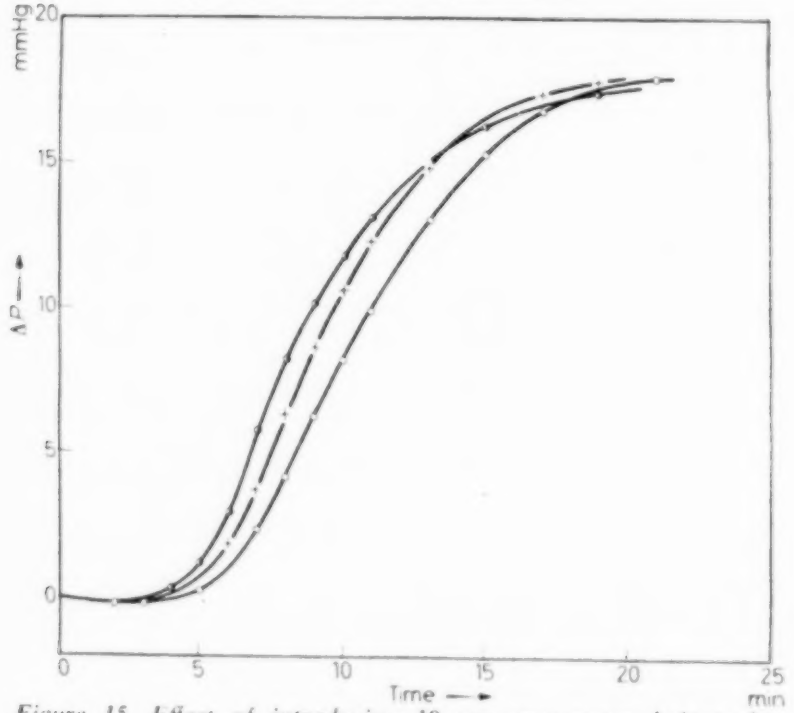

Figure 15. Effect of introducing 10 per cent water before the admission of reactants, conditions as for Figure 13. ○ *Reaction in the absence of water;* + *Water premixed with reactants;* ◑ *Water introduced before reactants*

The effect of the addition of inert gas in a vessel coated with potassium chloride—The rate of reaction of an equimolecular mixture of methane and oxygen (350 mm Hg, 500°C) was also followed in a reaction vessel coated with potassium chloride. Analysis of the product chilled at various stages of the reaction showed the presence of formaldehyde only. The experiment was repeated for a mixture formed by adding 250 mm Hg nitrogen to 350 mm Hg ($CH_4 + O_2$) mixture. The rate of reaction was considerably greater in the presence of nitrogen. Analysis of the products for intermediates showed complete absence of hydrogen peroxide, though formaldehyde was formed in similar concentrations to those previously obtained. While the increase in the rate of reaction (maximum) on adding 80 per cent nitrogen in a clean *Pyrex* vessel was 1·43-fold, the increase caused by the addition of 71·4 per cent nitrogen in a vessel coated with potassium chloride was 2-fold. Thus the diluent seems to increase the reaction rate more in a vessel coated with potassium chloride, presumably by reducing the access to the surface.

DISCUSSION

General considerations—For many years, there has been general agreement that the primary chains in the oxidation of methane consist of the reactions:

$$OH + CH_4 \longrightarrow CH_3 + H_2O \quad \ldots . [1]$$

$$O_2 + CH_3 \longrightarrow (CH_3OO) \longrightarrow OH + HCHO \quad \ldots . [2]$$

Argument has centred mainly on the mode of initiation and on the reactions which lead to the acceleration of the rate. An occasional reaction of the type

$$CH_4 + O_2 \longrightarrow HO_2 + CH_3, \quad \ldots . [3]$$

probably on the surface, conveniently accounts, amongst other possibilities, for the initial process. Surface initiation is indicated by the complete absence of reaction in the gold vessel at 460° to 500°C and by the heterogeneous oxidation of methane which can occur at active surfaces. The acceleration mechanism, however, is uncertain. As a consequence of Bone and Gardner's observation that the concentration of formaldehyde increased exponentially during the induction period (the period during which no pressure rise occurs), it has been assumed that the slow oxidation of this compound gives rise to radicals which attack methane molecules, so that the number of chains is gradually increased—a process usually referred to as 'degenerate branching'. The results presented here clearly confirm this general interpretation, since it has been shown, in a variety of experiments, that the autocatalysis depends, not merely on the presence of critical amounts of formaldehyde, but on conditions which permit the oxidation of the formaldehyde by a suitable mechanism.

The mechanism of the autocatalysis has usually been based on the intervention of OH radicals. B. LEWIS and G. VON ELBE[11], for example, suggested the following set of reactions:

$$HCHO + O_2 \longrightarrow HCO.OOH \quad \ldots . [4]$$

$$HCO.OOH \longrightarrow HCO.O + OH, \quad \ldots . [5]$$

the surface being supposed to affect the reaction by destroying OH radicals. The difficulty of controlling the nature and activity of the surface was believed to account for the differences between the results of different workers. In general, however, the mechanism appeared to explain the main features of methane oxidation.

In recent years, the situation has required further investigation following two developments. One of these was the report by G. J. MINKOFF and K. C. SALOOJA[12] that hydrogen peroxide could be isolated during the reaction, its concentration increasing exponentially to a maximum at the time of maximum rate. This suggested that other intermediates beside formaldehyde might be controlling the rate. At about this time, Hoare and Walsh[5] reported that the autocatalysis could be eliminated by coating the reaction vessel with lead oxide. G. H. N. CHAMBERLAIN, D. E. HOARE and A. D. WALSH[13] have argued, very convincingly, that the degenerate branching reaction cannot involve H, O, OH, or HCO, since these would all react in the gas phase before they reached the walls and should therefore lead to autocatalysis, even in spite of increased destruction at the surface. The only satisfactory alternative is that HO_2 (or possibly HCO_3) attacks methane and leads to secondary chains in reactions such as

$$HO_2 + CH_4 \longrightarrow H_2O_2 + CH_3 \qquad \ldots . [6]$$

This hypothesis has been further supported by the effects of surface treatment on the kinetic behaviour (Hoare and Walsh) observed by following the rate of pressure change, and also in the work described in this paper by analysing the peroxide content in the products and following the effects of different surfaces on it. A hydroxyl radical mechanism would only be compatible with the results obtained if the peroxide consisted mainly of formyl hydroperoxide; careful search, however, has failed to reveal the presence of this compound in appreciable quantities. It is therefore concluded that the branching chain reaction involves either HO_2, H_2O_2 or both.

Surface effects—The effect of surfaces such as potassium chloride is clearly in accord with this conclusion. The assumed destruction of hydroxyl radicals on potassium chloride has been partly based on work such as that of W. V. SMITH[14], who studied the recombination of various radicals on coated wires and deduced that potassium chloride was particularly effective for catalysing recombination of hydroxyl radicals. However, K. J. LAIDLER and K. E. SHULER[15] pointed out that gas phase reactions were competing strongly. D. R. WARREN[16] found little or no liberation of heat when the products of an electric discharge through water vapour were passed over a thermocouple coated with potassium chloride. In similar experiments, C. H. TOWNES and coworkers[17] measured the concentration of hydroxyl radicals by a microwave technique and confirmed that they did not recombine efficiently on a potassium chloride surface. The destruction of HO_2 radicals on such surfaces, on the other hand, has been established almost conclusively by studies of the hydrogen–oxygen reaction, *e.g.* by R. N. PEASE[18], B. LEWIS and G. VON ELBE[19], A. C. EGERTON and D. R. WARREN[20], G. DIXON-LEWIS, J. W. LINNETT and D. F. HEATH[21]. Conse-

quently, the features of the slow oxidation of methane on a potassium chloride or alkaline surface agree well with the suggestion that the autocatalysis due to HO_2 is eliminated: no peroxide being found, while chains involving HCHO and OH are not greatly affected. The relative importance of the contributions of the two sets of chains is discussed below. Qualitatively similar results are obtained with lead oxide surfaces. The destruction of some kind of radicals at a potassium chloride surface is also indicated by the greater acceleration caused by nitrogen in vessels coated with potassium chloride than in those treated with hydrofluoric acid.

On surfaces treated with boric oxide and hydrofluoric acid, HO_2 is not destroyed, but is converted into H_2O_2, which is released into the gas phase, where new chains are initiated by the OH radicals formed by dissociation of the H_2O_2 (see, for example, Egerton and Warren[20]). The exact mechanism of the wall reaction has not yet been elucidated, although various suggestions have been made. Warren, as a result of a study of the effect of a large number of surfaces on the kinetics of the H_2–O_2 reaction[16], concluded that the chain breaking efficiency was a function, not of the individual ions present, but of the alkalinity. This was illustrated particularly by the series H_3PO_4–KH_2PO_4–K_2HPO_4–KOH, in which the efficiency increased from zero to a maximum. Chain destroying salts such as potassium chloride were supposed to be capable of partial hydrolysis to potassium hydroxide at the reaction temperatures.

Warren's main deduction agrees well with the observation by Cheaney and Walsh that treatment of surfaces with hydrofluoric acid leaves a unimolecular film of silicic acid, and that the latter acid is directly responsible for the low HO_2 destruction efficiency. The acid, however, is stated to be partly dehydrated at these temperatures, and heat treatment is presumed to complete the dehydration and so increase the destruction efficiency. The effect of successive reactions in conditioning the surface can then be explained in terms of chemisorption of water (or of OH and H) at the surface (K. C. Saloója[22]) until the latter is fully hydrated. Experimental evidence is also provided in *Figures 14* and *15* which show the increased acceleration observed when water vapour is introduced into the reaction vessel, at the reaction temperature, before instead of with the reactants. Activated chemisorption is indicated because sufficient water was clearly not adsorbed at room temperature when the vessel was being rinsed free of hydrofluoric acid. Two other results support the general conclusion regarding the role of the surface. Firstly, the decrease in rate found when a vessel treated with hydrofluoric acid was stored unused for twenty weeks is presumably related to the well-known migration of metal ions from the body of the glass into the surface. Secondly, the absence of any effect of hydrofluoric acid on kinetics with soda glass surfaces is explained by the formation of sodium silicate, which is soluble and would therefore be washed away. This was demonstrated by Cheaney and Walsh, who removed the silicic acid film by washing with sodium hydroxide the silica surface cleaned with hydrofluoric acid. Thus, a considerable body of evidence now supports the correlation of the HO_2 destruction efficiency with the acidity or alkalinity of the surface.

Under conditions in which the surface does not destroy HO_2, but converts it into H_2O_2, it would be expected that diameter and inert gas influences would become less marked (though not zero, since there will be a small loss in the number of chain carriers). For added gases, this agrees with the results presented here and with those of Hoare and Walsh. The small effect of increasing the vessel diameter from 30 to 70 mm is also, at first sight, in agreement. However, even in aged vessels, the destructive power of the surface towards HO_2 (Norrish and coworkers) hardly showed itself as a diameter effect with vessels wider than 30 mm, so that the lack of effect in the present work may not be significant. An independence of vessel diameter in vessels treated with hydrofluoric acid has also been reported for the oxidation of ethane, by P. SADOWNIKOW[23].

Induction period—One of the main results of the present work[5] is that, while the concentration of H_2O_2 increases exponentially, that of formaldehyde at first increases more rapidly than that of H_2O_2, but at an almost constant rate. The concentrations of each then pass through a maximum and diminish continuously. This differs considerably from the findings of Bone and Gardner[7], who detected no formaldehyde after a third of the induction period, and only traces after two-thirds; after this stage, they found that the formaldehyde concentration rose rapidly but attained a steady value. It is of interest to examine this difference in the light of the knowledge that their surfaces, unlike surfaces treated with hydrofluoric acid, destroyed HO_2.

Confirmation of the present results is provided by L. SLOTIN and D. W. G. STYLE[24], who followed the concentration of formaldehyde in a silica vessel *in situ* by ultra-violet spectroscopy. They reported both the rapid rise and the eventual decrease. At first sight, the difference between these observations and those of Bone and Gardner could be ascribed to the less destructive surface permitting the more rapid oxidation of the formaldehyde and decreasing the concentration after the maximum rate was reached. The detection of some hydrogen under our conditions, but not under those of Bone and Gardner, appears to support this interpretation. However, another explanation is required as, during the induction period, the formaldehyde concentration expressed as a fraction of that at the end of the induction period, was greater, and not less, with vessels treated with hydrofluoric acid.

Of greater significance is the difference between the equations expressing the kinetic behaviour of the oxidation of methane under the two sets of conditions. Thus, while Bone and Gardner observed (as also did Norrish and Foord, and R. G. W. NORRISH and J. D. REAGH[25]) a period during which the overall rate of reaction was constant with aged surfaces, surfaces treated with hydrofluoric acid led to autocatalysis[3,5]. A kinetic treatment of the steady state reaction has been given by Norrish and Foord in terms of the degenerate branching chain theory. Essentially, their primary chains consisted of

$$A + CH_4 \longrightarrow B + H_2O \qquad \text{IV } k_4 \text{ (their notation)}$$

$$B + O_2 \longrightarrow HCHO + A \qquad \text{V } k_5$$

Secondary chains are formed by

$$HCHO + O_2 \longrightarrow \text{Prods.} + A \qquad \text{III } k_3$$

$$\text{and } HCHO + A \longrightarrow \text{Prods.} \qquad \text{VII } k_7$$

The growth of formaldehyde (F) is given by

$$\frac{d}{dt}(F) = \theta + \phi(F)$$

where θ is the rate of formation by the primary process, and $\phi(F)$ that by the secondary branching chains. Since the velocity was unobservable at the beginning of the induction period, Norrish and Foord deduced that the rate of formation by the primary process was negligible compared with the rate of formation from centres generated in the later stages. (F) was thus only proportional to $\exp(\phi t)$. According to Semenoff,

$$\phi(F) = k_3(\nu - 1)(O_2)(F) - R,$$

where ν is the chain length of the primary chains, and R is the rate of removal of F. At the time of maximum rate, $\phi(F)$ becomes zero as a result of the increase in R caused by the growth of (A). By making some assumptions about the mechanism, it was possible to predict the observed kinetic features, including the effect of vessel diameter, and the constancy of the ratio $(F)/(CH_4)$.

In vessels treated with hydrofluoric acid the scheme proposed by Hoare and Walsh showed the possibility of an additional mode of generating new chains. This is a consequence of reaction 6, in which hydrogen peroxide is formed. As these authors indicated, the conditions of pressure and temperature are similar to those in which the oxidation of hydrogen proceeds. It is therefore possible to apply to the present system the deduction by Egerton and Warren, that H_2O_2 generated chains by its decomposition. Owing to the constancy of their term b, from 8 to 160 mm pressure, the decomposition was thought to be unimolecular,

$$H_2O_2 \longrightarrow 2OH \qquad \ldots\ldots [7]$$

This is supported by the recent work of P. A. GIGUÈRE[28], who observed homogeneous, first-order decomposition, unaffected by packing, from 400° to 600°C. It therefore seems that, while Norrish and Foord's scheme accounts for the results in aged vessels, the gas phase decomposition of the hydrogen peroxide formed in vessels treated with hydrofluoric acid leads to an additional mode of branching. Formally, this can be represented as:

$$\text{Primary chains} \begin{cases} A + CH_4 \longrightarrow B + H_2O & \ldots\ldots (a) \\ B + O_2 \longrightarrow HCHO + A & \ldots\ldots (b) \end{cases}$$

$$\text{Secondary chains} \begin{cases} HCHO + (A, O_2\ etc) \longrightarrow C + \text{Prods.} & \ldots\ldots (c) \\ C + CH_4 \longrightarrow B + D & \ldots\ldots (d) \\ D \longrightarrow A + A & \ldots\ldots (e) \end{cases}$$

(Clearly, $A = OH$, $B = CH_3$, $C = HO_2$, $D = H_2O_2$).

Mathematical analysis of this system would be complicated, but a number of qualitative deductions can be made.

Firstly, direct experimental evidence of the presence of H_2O_2 in the reaction system in the early stages is provided by the small pressure decrease reported in the 'induction period'[5]. If it is assumed that the drop is due to the contraction accompanying the overall reaction

$$CH_4 + 1\tfrac{1}{2}O_2 \longrightarrow HCHO + H_2O_2$$

(a suggestion for which the authors are grateful to Drs Hoare and Skirrow), then the magnitude of the drop is commensurate with the quantity of hydrogen peroxide isolated at this stage of the reaction. Significantly, the contraction is only observed in vessels treated with hydrofluoric acid.

Secondly, the isolation of more formaldehyde than peroxide during the induction period is in agreement with the assumption that the rate of oxidation of formaldehyde is less than the rate of unimolecular decomposition of hydrogen peroxide. Consequently, the radicals produced by the latter have a more powerful influence on the overall rate than do the radicals, fewer in number, which arise through the former. It follows that there is a much closer connection between the rate of oxidation of methane and the concentration of hydrogen peroxide, as shown by the exponential, and concurrent, increase of both these quantities with time, than between the rate and the concentration of formaldehyde. The smaller dependence on the methane concentration reported by Hoare and Walsh could be a consequence of this, and it may be predicted that, at the limit, explosion will have a branched chain character instead of being of the thermal type observed by Norrish and Foord in aged vessels.

The theory presented here is also in accord with the observation that the maximum rate is reached at an earlier stage with HO_2-destroying surfaces than with surfaces treated with hydrofluoric acid (see also reference 3). When the 'basic' type of degenerate branching (Norrish) can be reinforced by the H_2O_2 branching system, the rate will clearly continue to accelerate for a greater proportion of the total reaction, as the number of radicals will considerably exceed those produced by the basic mechanism only. It is, in fact, this difference in the contributions made by the two modes of degenerate branching which ensures that the present explanation does not contradict Chamberlain, Hoare and Walsh's deduction that the autocatalysis was due to HO_2 and not to OH. Both contribute, but the branching introduced by HO_2 is of a higher kinetic order than that introduced by OH.

The same result can be deduced by considering the rate of pressure change with a potassium chloride surface. If all the autocatalysis was eliminated, it could be suggested that the reaction followed was the primary one (*i.e.* reactions 1 and 2), and that the induction period represented the time in which the straight chain system developed its maximum rate. This cannot be so, however, as no pressure change is involved. Some formaldehyde molecules must therefore be oxidized, and additional chain carriers are thus being formed, as in Norrish's original scheme.

Finally, some consideration must be given to the effect of surfaces on the oxidation of formaldehyde (in the absence of methane). Although the evidence is rather scanty, it would appear (Lewis and von Elbe[19]) that

surfaces freshly cleaned with nitric acid, or in the presence of mercury vapour, destroy peroxidic intermediates and lead to simple, second-order kinetics, the maximum rate being immediately attained. Aged surfaces lead to short induction periods when the reaction is followed by observing the pressure change. M. D. SCHEER[27] however has shown, by mass spectroscopic analysis, that formaldehyde is in fact reacting rapidly, with no pressure change, to give various peroxides. According to F. F. SNOWDEN and W. G. STYLE[28], on the other hand, treatment with hydrofluoric acid gave very long induction periods, followed by slow rates of pressure change; successive reactions became more rapid. In the absence of analytical data, it seems difficult to draw any firm conclusions, particularly since no mechanism has yet become generally accepted (D. W. G. STYLE, E. C. A. EGERTON and D. SUMMERS[29]; also Scheer[27]). It would seem useful, in fact, to re-examine the formaldehyde oxidation with various surfaces in the light of recent developments. In any case, since the concentration of methane is always much greater than that of formaldehyde, the conditions in the oxidation of formaldehyde alone and in the presence of methane are not strictly comparable, since those two compounds would compete for chain carriers. Further complications may be introduced by the oxidation of carbon monoxide to carbon dioxide.

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Some Properties of Formaldehyde Flames

A. R. HALL, J. C. MCCOUBREY and H. G. WOLFHARD*

Some properties of the flames of formaldehyde with oxygen and nitric oxide, notably the spectra and the oxygen index, are reviewed and compared with those of its main thermal decomposition products, i.e. carbon monoxide and hydrogen on the one hand and of organic bodies on the other. Some deductions are made about the combustion mechanisms with the formaldehyde flames. The usefulness of spectral data obtained with flames of a relatively simple compound, such as formaldehyde, in helping to understand the combustion of more complex compounds, is illustrated for flames of ethyl nitrate and methyl nitrite with oxygen.

FORMALDEHYDE is an important intermediate product in many flame reactions, especially those with the self-decomposition flames of some compounds containing organic nitrogen[1-3], but its combustion has received little attention; this is no doubt partly due to the need to provide a constant and reproducible vapour supply of the monomer for burning stationary flames. Some observations with low pressure flames have, however, been reported and these are discussed together with a few new measurements.

The manner in which spectral information from simpler systems may be used to help interpret spectra given by more complex systems is illustrated with spectra of flames of formaldehyde burning with oxygen and with nitric oxide and of ethyl nitrate, methyl nitrite and nitromethane burning with oxygen.

FORMALDEHYDE–OXYGEN FLAMES

Monomeric formaldehyde was produced in an electrically heated glass vessel from para-formaldehyde; the connections and the burner were kept above about 120°C to prevent polymerization of the formaldehyde. It was possible to get a very steady flow of gas; the mass flow was difficult to measure, but this was not serious as most measurements did not depend critically on this mass flow.

Formaldehyde burns very readily with oxygen at low pressure. (For details of the low pressure burner apparatus see Reference 4). The spectrum consists of very weak C_2 bands, which occur only in fuel-rich mixtures, weak CH bands and extremely strong OH bands besides weaker CO flame bands (see *Figure 1A*). The OH bands are much stronger in the reaction zone than in the burnt gas[5,6] and, in this respect, the spectrum resembles that of a hydrocarbon–oxygen flame in which OH bands are also subject to a high excitation temperature in the reaction zone, a property not shown by hydrogen and carbon monoxide flames[5,6]. A further property of hydrocarbon–oxygen flames is the excess electronic excitation of added

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metal vapours, such as iron, in the reaction zone. Formaldehyde flames do not show this abnormality and iron lines seem to be thermally excited[6]. OH bands in formaldehyde are also free from the high rotational temperature which is otherwise always associated with the excess electronic excitation of OH on hydrocarbon–oxygen combustion[5]. These properties,

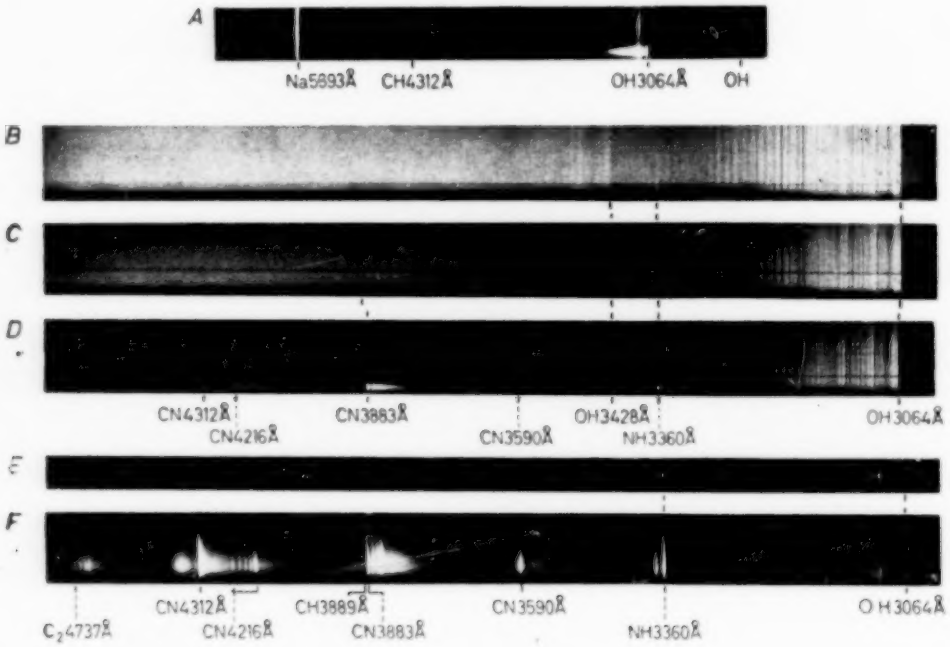

Figure 1. The records are emission spectra of flat, pre-mixed flames stabilized on a burner and viewed end-on. The lower edge of each spectrum corresponds to the leading surface of the flame. The gas mixtures were all near stoichiometric. The spectra were all obtained with a Hilger medium spectrograph (quartz set) except for A which was obtained with a Hilger Raman, F/4, spectrograph (quartz set)

	Burner diam. cm	*Pressure*	*Plate*	*Slit mm*	*Exposure min*	*sec*
A *Formaldehyde–oxygen*	1·5	2 *cm* Hg	*HP* 3	0·1	4	
B *Formaldehyde–nitric oxide*	2	*atm*	*HP* 3	0·03		40
C *Methyl alcohol–nitric oxide*	1·5	*atm*	*HP* 3	0·03	3	
D *Methane–nitric oxide*	1	*atm*	*HP* 3	0·03		30
E *Methyl nitrite–oxygen*	2	2·2 *cm* Hg	*Zenith*	0·03	5	
F *Ethyl nitrate–oxygen*	2	2·3 *cm* Hg	*Zenith*	0·03	5	

summarized in *Table 1*, show the interesting position formaldehyde possesses between hydrogen and carbon monoxide on the one hand and organic fuels, especially hydrocarbons, on the other. Methyl alcohol and formic acid are also included in *Table 1* for comparison. In reading this *Table* it has to be realized that the properties listed are present in many flames, to a greater or lesser degree, and the table is therefore somewhat idealized. However, if a 'yes' or a 'no' is entered very large differences are in fact observable.

It is clear from this table that the combustion of formaldehyde cannot be wholly explained on the assumption that, as formaldehyde is generally understood to break down homogeneously mainly into hydrogen and carbon monoxide on heating, it would behave like an equimolar mixture of those gases in flames. Such a mixture would show neither the observed excess

Table 1. Nature of OH *emission and of excitation of* Fe *lines in flame spectra of formaldehyde and allied fuels with* O_2, NO *and* N_2O

Fuel/oxidizer system	OH *emission much stronger in reaction zone than in burnt gas*	*High rotational temperature of* OH *in reaction zone*	*High electronic excitation of* Fe *lines*	*References*
H_2/O_2	*No*	*No*	*No*	5 *and* 6
H_2/NO	*No*	*No*	*No*	7
H_2/N_2O	*Yes*	*Moderately high*	*Moderately high*	5 *and* 6
CO/O_2	*No*	*No (from traces of* H_2O*)*	*No*	5
C_2H_4, CH_4 etc/O_2	*Yes*	*Yes*	*Yes*	5
C_2H_4, CH_4 etc/NO	*No*	*No*	*No*	7
C_2H_4, CH_4 etc/N_2O	*Yes*	*Slightly too high*	*Unknown, probably too high*	5 *and* 7
H_2CO/O_2	*Yes*	*No*	*No*	5 *and* 6
H_2CO/NO	*No*	*No*	*Presumably no*	
H_2CO/N_2O	*Yes*	*Unknown; presumably no*	*Unknown*	5
CH_3OH/O_2	*Yes*	*Slightly too high*	*Yes*	5 *and* 6
CH_3OH/N_2O	*Yes*	*No*	*Presumably yes*	5
CH_3OH/NO	*No*	*No*	*Presumably no*	

OH radiation in the reaction zone nor the weak emission of C_2 and CH bands. Recent experiments on the pyrolysis of formaldehyde, however, suggest that the molecule breaks down homogeneously by a chain mechanism and that methyl alcohol is an important product[8]. In the oxidation of formaldehyde in aged vessels, formic and performic acid have been found as intermediates[9]. The spectrographic data in *Table 1* show that formaldehyde retains some characteristics of higher organic fuels and that methyl alcohol has more 'organic' character than formaldehyde; this may seem inevitable from the presence of the CH_3 group, but such hydrocarbon groupings are not the sole determinants of this. For example, the writers have found that methyl bromide–oxygen flames emit C_2 and CH bands much more strongly than methyl alcohol–oxygen flames.

Hydrogen and carbon monoxide differ from organic fuels in a further important flame property. This is the limiting oxygen index of combustion, which is defined as the ratio $O_2/(O_2 + N_2)$ for the mixture containing the maximum amount of nitrogen as diluent which will still propagate a flame. The limiting oxygen index can be derived from limit determinations undertaken by the Bureau of Mines (U.S.A.) where inert gas was added to premixed flames until flame propagation ceased[10]. The second column of

Table 2 lists these values and it is clear that the values for hydrogen and carbon monoxide are only about half those for hydrocarbons.

The oxygen index of formaldehyde cannot be measured in the same way. However, diffusion flames can be used for such determinations[11] although values so derived are less reliable. The procedure used was to burn a fuel

Table 2. Limiting oxygen index of formaldehyde and some allied fuels

Fuel	*Limiting oxygen index from premixed flames (stoichiometric mixture)*	*Limiting oxygen index from diffusion flames with burner preheated to 150°C*
Hydrogen	0·056	0·053
Methane	0·130	0·147
Ethane	0·118	0·13
Carbon monoxide	0·069	0·084
Formaldehyde		0·071
Hydrogen + carbon monoxide equimolar		0·057
Propane		0·13
Methyl alcohol		0·10
Formic acid		*about* 0·12
Acetaldehyde		0·12
Carbon monoxide + methane equimolar		0·135

as a diffusion flame in air and progressively dilute the 'air' with nitrogen until the flame ceased to burn. With formaldehyde the delivery tube and burner had to be heated to prevent polymerization of monomeric formaldehyde, and to get comparable oxygen indices for hydrogen and organic fuels, these were also determined under the same conditions. These results are given in column three of *Table 2*. Formaldehyde has a limiting oxygen index close to, but not identical with, that expected for a mixture of hydrogen and carbon monoxide; the value is far below that of any other organic fuel.

FORMALDEHYDE–NITRIC OXIDE FLAMES

It is important to know whether formaldehyde plays an active role in nitric oxide reduction in flames of organic compounds containing nitrogen. Hydrogen and carbon monoxide are very inefficient in this respect and, in hydrogen as well as in carbon monoxide–nitric oxide flames, it is known that nitric oxide breaks down by thermal decomposition prior to oxidation reactions. This process is only possible because of the very high temperatures of these flames[7]. However, this is not the only mode of decomposition of nitric oxide in flames, since, for example, ammonia–nitric oxide flames burn readily at much lower temperatures than hydrogen–nitric oxide flames, probably due to radical reactions involving NH_2 and NH formed during the ammonia breakdown. Such radical reactions need less activation energy and are therefore more efficient than the thermal decomposition of

nitric oxide. Hydrazine is even more efficient in this respect and burns with nitric oxide down to extremely low pressures[12], whereas hydrogen–nitric oxide, for example, does not. It is also striking how easily methyl bromide burns with nitric oxide, although this flame has a much lower flame temperature than the corresponding hydrogen or methane flame. This may well be due to the ability of organic radicals to reduce nitric oxide.

Formaldehyde was therefore burnt with nitric oxide at 1 atm as a premixed flame on a 2 cm diameter burner. *Figure 1B* shows the spectrum, which is identical with that of a hydrogen–nitric oxide flame. CN bands, which always occur in hydrocarbon–nitric oxide flames[7], are absent in the formaldehyde flame. Also, the formaldehyde flame cannot conveniently be burnt at low pressures because the quenching diameters are too large. On this basis, methyl alcohol is nearly as inefficient as formaldehyde in combustion with nitric oxide, although rather weak CN and NH bands are present in the flames at atmospheric pressure, as shown in *Figure 1C*; the absence of these bands would suggest that little or no methyl alcohol is formed by the decomposition of formaldehyde in the formaldehyde–nitric oxide flames. Formic acid could not be burnt with nitric oxide at all. The spectrum of a methane–nitric oxide flame can be seen in *Figure 1D*, for comparison; here, the CN and NH bands are very prominent in the reaction zone.

Flames of formaldehyde burning with nitrogen dioxide also resemble those of hydrogen and carbon monoxide in giving only partial combustion, with nitric oxide passing through the reaction zone undecomposed. The second reaction zone which occurs on hydrocarbon–nitrogen dioxide combustion[7] is missing. With hydrocarbons it is in this second zone that nitric oxide normally reacts and gives rise to strong CN and NH bands. Very weak OH bands may, however, just be detectable for formaldehyde flames very rich in nitrogen dioxide.

On this evidence, there is no reason to believe that formaldehyde reduces nitric oxide by a radical mechanism. Formaldehyde, therefore, is not likely to be responsible for the partial reduction of nitric oxide, which is observed in self-decomposition flames such as methyl nitrite[2] or ethyl nitrate[1].

DISCUSSION

It is significant that the oxygen indices, and consequently the limit temperatures, of hydrogen and carbon monoxide are much lower than for hydrocarbons; this shows that the breakdown of a hydrocarbon is a major resistance to its burning. Methyl alcohol has a lower oxygen index and limit temperature than hydrocarbons, though the values are still much higher than those for hydrogen and carbon monoxide. It is only formaldehyde which behaves almost as if it were an equimolar mixture of the two gases; its decomposition does not therefore seem to retard the combustion process to a large extent.

The spectral emission of formaldehyde–oxygen flames, however, shows clearly that radical reactions are occurring which would not be expected in hydrogen and carbon monoxide mixtures. CH and very weak C_2 bands

are present in the formaldehyde–oxygen flame. More important is the non-thermal excitation of the OH ($^2\Sigma$) state, which might be due to the reaction

$$CH + O_2 \longrightarrow CO + OH\ (^2\Sigma).$$

This fact can be very helpful because it distinguishes the formaldehyde spectrum from the spectrum of hydrogen flames, as well as from the spectra of hydrocarbon flames, which exhibit further non-thermal aspects not found in formaldehyde flames (see *Table 1*).

The presence of C_2 and CH bands also throws light on the formation of these radicals. It is hardly conceivable that formaldehyde polymerizes prior to oxidation to form a C–C band from which a C_2 molecule might finally be derived. Nor does hydrocarbon polymerization in flames usually lead to C_2 formation, as evidenced by the facts that the very hot self-decomposition flame of acetylene does not emit C_2 or CH bands[13] and hydrocarbon–chlorine flames do not emit any bands whatsoever[11]. A similar conclusion has recently been reached by R. E. FERGUSON[14] who found that the C_2 bands in acetylene flames cannot have their origin in the carbon–carbon bond of the acetylene molecule. It seems therefore that C_2 molecules are formed in radical reactions common to hydrocarbon and formaldehyde combustion. Reactions involving HCO are a possible source of C_2 and CH radicals. Although HCO bands do not occur in formaldehyde flames this does not rule out the above suggestion, because HCO bands are quite weak in other flames where C_2 and CH bands are many times stronger than in the formaldehyde flame. HCO bands may in fact have a very small transition probability.

The reactions in nitric oxide flames occur generally at a much higher temperature level than in oxygen flames[7], unless organic radicals are available at an early stage in the reaction zone. Formaldehyde may thus have ample time to decompose into hydrogen and carbon monoxide before reduction of nitric oxide occurs. The formaldehyde–nitric oxide flame therefore resembles hydrogen and carbon monoxide flames with nitric oxide in every detail. Formic acid does not burn with nitric oxide presumably because the adiabatic flame temperature is too low for the thermal decomposition of nitric oxide. Again, methyl alcohol shows properties approaching those of hydrocarbons. Methyl bromide burns so readily with nitric oxide that it is probably radicals such as CH_3 and CH_2 which help to decompose nitric oxide and in so doing form CN and NH radicals which are easily observable in such flames with methyl bromide and hydrocarbons but not with formaldehyde. In this respect it is significant that, whereas hydrogen, carbon monoxide and formaldehyde have a lower limit temperature than hydrocarbons when burning with oxygen, *i.e.* burn more easily, this situation is reversed with nitric oxide combustion.

The usefulness of the above type of spectral data in helping to understand the processes in the combustion of more complex systems can be demonstrated with results from the combustion of methyl nitrite, nitromethane and ethyl nitrate with oxygen which are to be published in full elsewhere[12]. *Figures 1E* and *1F* show the spectra of stoichiometric methyl nitrite and

ethyl nitrate–oxygen flames respectively. Both flames were investigated under the same conditions. The stoichiometric methyl nitrite–oxygen flame emits weak CH, CN and NH bands. These bands are much weaker than those with the ethyl nitrate–oxygen flame and have not recorded in the print of the spectrum (*Figure 1E*) in which, for purposes of comparison, the head of the OH band has been made of equal strength to that of the ethyl nitrate spectrum (*Figure 1F*). Both flames show OH bands which occur in the reaction zone but not in the burnt gas above. The OH band cannot therefore have its origin in the combustion of hydrogen or carbon monoxide with oxygen or of any fuel with nitric oxide; however, formaldehyde, methyl alcohol and hydrocarbon–oxygen reactions give this effect. *Figure 1E* shows clearly that the ethyl nitrate reaction zone has a high rotational temperature of OH whereas the methyl nitrite has not (*Figure 1F*). From this it follows that in the ethyl nitrate–oxygen flame OH is emitted during the reaction of larger organic molecules or fragments with oxygen, whereas in the methyl nitrite flame OH emission is due to reaction of formaldehyde and/or methyl alcohol with oxygen. Nitromethane behaves very similarly to ethyl nitrate. Methyl nitrite flames do not show any OH emission at all[2] unless exploded in a closed vessel where flame temperatures are much higher[12]; no CN or CH bands are emitted, however, which shows that the reaction is mainly due to reactions of hydrogen and carbon monoxide, or formaldehyde, with nitric oxide. This list of applications is not complete but shows that the detailed knowledge of the spectra of simpler flames can lead to an understanding of the processes in more complicated flames.

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Burning Velocities of Hydrogen Cyanide in Air and in Oxygen

L. COHEN and P. SIMPSON

The burning velocities of hydrogen cyanide in air and in oxygen have been measured for the first time. Maximum velocities of 55 cm/sec in air and 540 cm/sec in oxygen were observed.

SO FAR as can be ascertained no measurements have previously been made of the burning velocities of mixtures of hydrogen cyanide in air or oxygen.

EXPERIMENTAL PROCEDURE

The method employed, using a nozzle burner, was that previously described[1]. The combustible mixture was obtained by bubbling either air or oxygen, obtained from high pressure cylinders, through liquid hydrogen cyanide of commercial quality, having a purity better than 98 per cent, most of the impurity being stabilizing agent. The flask containing the hydrogen cyanide was kept in an enclosure which was maintained at a constant temperature of 2° or 3° below the boiling point of the cyanide (26°C). The vapour-laden gas stream was mixed, when necessary, with a stream of pure air or oxygen to give the appropriate mixture strength. The mixture passed through a flame trap to the burner tube, at the end of which was a burner nozzle of 3·2 mm diameter for the air mixtures and 1·53 mm for the oxygen mixtures.

A flame trap consisting of a tube filled with glass beads was found to be adequate for the air mixtures but completely useless when oxygen was

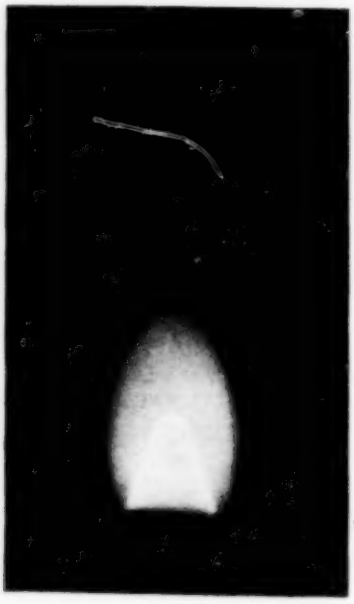

Figure 1. Photograph of hydrogen cyanide–air flame

used. For the latter the only satisfactory device was found to be a sintered metal disk placed in the feed pipe, which entered the burner tube at right angles, and a paper bursting disk fitted to the lower end of the burner tube[2].

The composition of the gas mixture was determined by washing a known volume with dilute caustic soda. The decrease in volume was the volume of hydrogen cyanide.

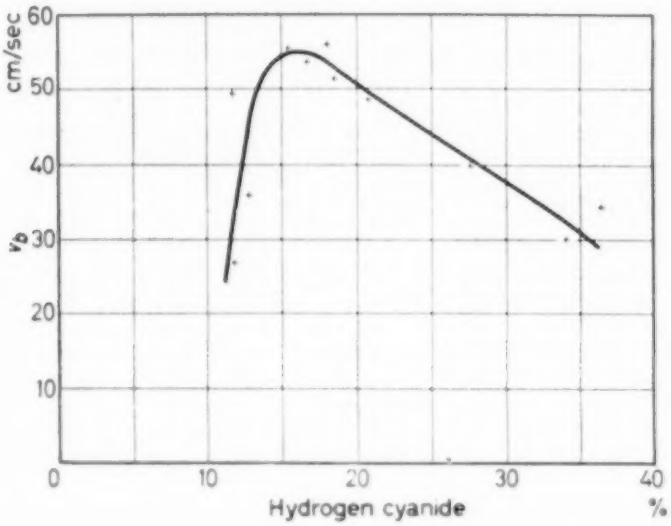

Figure 2. Burning velocities of mixtures of hydrogen cyanide and air

RESULTS

No difficulty was experienced in obtaining stable flames over quite a wide range of mixture compositions. In appearance the air flames have normally three distinct zones, an inner cone of a violet colour, a bright yellow central mantle and a pale blue outer mantle. A typical example is shown in *Figure 1*. The flames with oxygen have a similar appearance except that in many the central mantle becomes very small and has the effect, in the photographs of the flame, of thickening the primary reaction zone, thus increasing the difficulty of measuring the burning velocity.

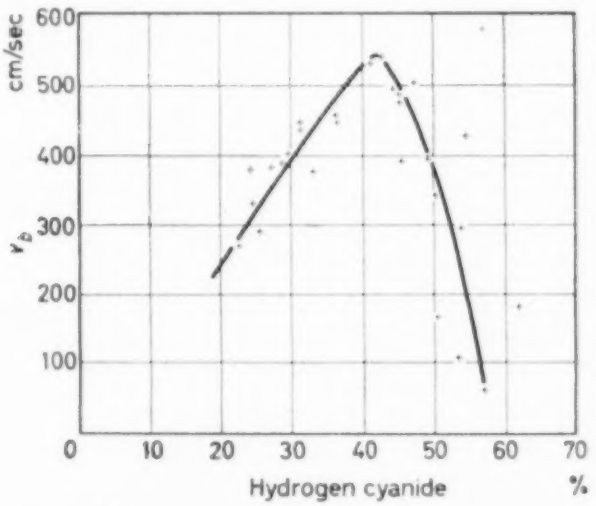

Figure 3. Burning velocities of mixtures of hydrogen cyanide and oxygen

The results of the burning velocity determinations are shown in *Figures 2* and *3* which give the variation of the burning velocity with concentration of hydrogen cyanide. In mixtures with air the maximum burning velocity is about 55 cm/sec at a concentration of about 16 per cent hydrogen cyanide. The stoichiometric concentration for complete combustion to carbon dioxide, nitrogen and water is 14·4 per cent.

In mixtures with oxygen the maximum burning velocity is about 540 cm/sec at a concentration of about 42 per cent hydrogen cyanide; the stoichiometric concentration is then 44·4 per cent.

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The Explosibility Characteristics of Coal Dust Clouds using Electric Spark Ignition

D. L. CARPENTER

Present knowledge of the effect of the various factors which govern the explosibility characteristics of coal dust clouds has been summarized. The theories of the mechanism of the ignition and self-sustained combustion of dispersed coal dusts have been discussed. The explosibility characteristics of a range of South Wales and certain English coals and the effect on these characteristics of variation of the oxygen content of the dispersion medium has been investigated. Possible explanations of the difference between the calculated and the observed maximum pressures have been given. Practical evidence supporting the theory that gas-solid oxidation is responsible for the initiation of propagated combustion has been obtained from an investigation of the effect on coal dust explosibility of (a) *the addition of admixed inert dust,* (b) *prior oxidation of the coal dust and* (c) *the blending of non-explosive and explosive dusts. It has been concluded that for all coal dusts the reaction initiating combustion and explosion is that between the coal particle surface and gaseous oxygen. The heat liberated will be supplemented, with medium and high volatile coals, by the burning of inflammable decomposition products around the coal particle giving, as a result, an increased rate of heat transfer and explosion velocity.*

THE FACTORS which govern the ease of ignition of coal dust clouds and the magnitude of the pressures developed in closed systems are numerous, while the true significance of these factors in relation to the mechanism and kinetics of ignition and propagated combustion of dust clouds is still rather vague. The variables which influence the explosibility of a dust cloud in a given apparatus include the chemical nature of the dust; the particle size, shape and surface characteristics of the dust; the concentration of dust in the cloud; the nature and energy of the igniting source; the oxygen content of the dispersion medium and the nature of the remaining constituents; the uniformity of dispersion of dust in the cloud; the fraction of the potential heat of the dust which is liberated during explosion and the temperature and pressure of the dust cloud before ignition. In addition, the possibility of heat loss due to the dissociation of combustion products at the flame temperature must be considered. Explosibility characteristics are interpreted as the maximum pressure, together with the maximum and average rates of pressure increase developed during the self-sustained combustion of dust clouds in a closed system. In addition, the minimum explosive dust concentration, the minimum energy required for ignition and the lowest oxygen concentration at which self-propagated combustion can be affected, may be used as criteria of explosibility. The experimental work described in this paper is confined to explosibility measurements and will not include the combustion characteristics of dust clouds in open systems which have been reviewed by the author elsewhere[1].

THE EFFECT OF THE VARIABLES WHICH GOVERN THE EXPLOSIBILITY OF COAL DUST

Chemical nature of dust

At one time it was generally accepted that an essential stage in the inflammation of any dispersed combustible dust was the evolution and combustion of the inflammable gases and vapours produced by the decomposition of the dust particles. This view though possibly correct in the inflammation of high volatile coal dusts, cannot be held when the inflammation of metal dust clouds is considered. The dust clouds of many metals are far more inflammable than coal dust clouds and yet the vapour pressures of the metals even at their ignition temperatures are very low. Even with coal dust inflammation some doubt exists as to whether the volatile matter of the coal acts as an explosion initiator.

I. HARTMANN, M. JACOBSON and R. P. WILLIAMS[2] measured the explosibility characteristics of the dusts of a number of American coals ranging from semi-anthracite to gas coals using the apparatus developed orginally by Hartmann[3]. They found that when using a standard concentration of 0·5 oz/ft.^{3} of a fraction of the coal dust passed through a 200-mesh Tyler sieve dispersed in air and ignited by sparks, the maximum pressure, average and maximum rates of pressure increase developed during explosion all increased with decrease in rank of the coal. The minimum explosive concentration and the minimum spark energy required for ignition were found to decrease with decrease in rank. The effect of coal rank on the explosibility of dusts dispersed in oxygen was found by these authors to be much less pronounced than that obtained using air dispersion. Decrease in rank beyond a volatile content of 15 to 20 per cent (d.m.m.f.) had practically no effect on any of the explosion characteristics in oxygen.

Particle size of dusts

G. S. RICE and H. P. GREENWALD[4] have shown that the upper size limit for coal dust explosibility is 0·5 mm. H. A. J. PIETERS and J. W. J. HOVERS[5] found that coal dust explosibility reaches a maximum in the particle diameter range 75 to 105 μ. G. J. O. ZONNERBERG[6] has stated that at particle diameters below 50 μ the explosibility of coal dust decreases. This decrease, he claims, is due to the poor dispersability of the finer particles. C. M. BOUTON and J. H. HAINER[7] studying the pressures developed during coal dust explosion found that the 0 to 10 μ and the 10 to 15 μ fractions of a coal dust produced lower explosion pressures than the 15 to 25 μ fraction. They suggested that this apparent anomaly is due to one or more of the following effects: variation of chemical composition with particle size for the finer dusts; preferential oxidation of the smaller particles and the possible agglomeration of these particles. In their laboratory study of the explosibility characteristics of American coals Hartmann, Jacobson and Williams[2] found that for suspensions of Pittsburgh coal dust in air both the minimum energy required for ignition and the minimum explosive concentration increased rapidly with increase in particle size up to a particle diameter of 100 μ. Larger particles could not be ignited in

air by electric sparks. The maximum pressure developed during the explosion of air dispersions of the dusts of these American coals were found to decrease with increase in particle size. Replacement of air by oxygen in the dispersal of the dusts enabled coal dusts of up to 500 μ particle diameter to be ignited by electric sparks while the effect of particle size variation on minimum ignition energy and minimum explosive concentration was much less pronounced in oxygen than in air.

Dust concentration

The lower explosive limit

The lower explosive limit (minimum explosive concentration) is the lowest dust concentration in the dust cloud which will support and propagate combustion initiated by an igniting source of specified energy. A theoretical expression for the lower explosive limit has been derived by G. JAECKEL[8] for the thermal ignition of dust clouds under constant volume conditions. It is assumed that one side of the combustion space is occupied by a plane hot surface of infinite area and that the heat flow occurs only in a direction perpendicular to the hot surface. The explosion of the dust cloud then starts by the heating and ignition of the dust particles in the air layer parallel to and adjacent to the hot surface. The heat produced during this combustion in turn heats and ignites the next dust–air layer and the combustion (explosion) is propagated in this way throughout the dust cloud. In lower limit mixtures there are just enough particles in each parallel dust–air layer to produce the heat required to bring the adjacent layer to its ignition temperature after allowing for the heat lost by radiation and conduction. Jaeckel states that neglecting heat losses the heat of combustion generated in unit volume of combustion space must at least equal the heat required to raise the temperature of the dust and air in unit volume to the ignition point of the dust.

$$\text{Thus} \quad pq = p(T-t)C_2 + (T-t)SC_1$$

$$p = \frac{(T-t)SC_1}{q-(T-t)C_2}$$

where p is the lower explosive limit of dust concentration; q is the heat of combustion of unit weight of the dust; T is the ignition temperature of the dust; t is the initial temperature of the dust cloud; S is the density of air at the initial temperature and pressure; C_1 is the specific heat of air at constant volume; and C_2 is the specific heat of the dust. This expression, derived for idealized conditions gives an approximate value only for the lower limit. In addition it over-simplifies the mode of heat transfer, does not allow for the possible dissociation of combustion products or the effect of the particle size of the dust. Jaeckel did show, however, that when the area of the ignition source approaches that of a point source within the dust cloud the lower explosive limit is much greater than the value obtained from the above theoretical expression.

Hartmann[9] has investigated the effect of type of ignition source on the lower explosive limit of coal dust. Using air dispersed suspensions of finely

pulverized coal dust Hartmann obtained a lower explosive limit of 0·035 oz/ft.^{3} when the ignition source was a continuous electric spark. The lower limit obtained for the same dust when ignition was initiated with the flame of a small quantity of gun cotton was 0·005 oz/ft.^{3}. Using the theoretical expression derived by Jaeckel[5], Hartmann calculated the lower explosive limit for the coal dust and obtained a value of 0·017 oz/ft.^{3}, *i.e.* much lower than the value 0·035 oz/ft.^{3} obtained with spark ignition.

Maximum explosibility

Available information on the effect of dust concentration on the maximum pressures developed, the maximum and average rates of pressure increase during coal dust explosions concerns the American coals studied by Hartmann, Jacobson and Williams[2]. Increase of dust concentration of a fraction that passed through a 200-mesh Tyler sieve, dispersed in air and ignited by sparks, resulted in an increase in the maximum pressure, the average rates and the maximum rate of pressure increase. Maximum values of these three characteristics were obtained at a dust concentration of 0·9 oz/ft.^{3}; further increase in concentration gave a decrease in explosibility. Theoretically it would be expected that the maximum explosive effect would be produced at a concentration such that the amount of dust involved was just sufficient to consume all the available oxygen. When the dust concentration is below this theoretical maximum pressure value the excess air absorbs part of the heat of combustion—whereas excess dust results in incomplete combustion. Hence it might be expected that the stoichiometric mixture possesses maximum explosibility. For a coal dust of composition 85 per cent carbon and 6 per cent hydrogen the stoichiometric mixture would require a dust concentration of about 0·11 oz/ft.^{3}. The actual maximum pressure concentrations determined by various workers are invariably much greater than the stoichiometric mixture concentration. The maximum pressure concentration of 0·9 oz/ft.^{3} for a Pittsburgh coal dust in air determined by Hartmann, Jacobson and Williams[2] has already been mentioned. V. C. Allison[10] and J. D. Morgan[11], in their laboratory experiments on coal dust explosibility found that the maximum explosive effect produced by coal dust occurs at concentrations of at least 0·5 oz/ft.^{3}. It has been suggested that this tendency of displacement towards excess combustible in dust explosions may be explained by the difficulty of raising the whole of the coal dust into homogenous suspension in air.

The upper limit of explosibility

Whereas there are difficulties in determining the lower explosion limit for coal dusts with accuracy, these difficulties become manifold when measurement of the upper limit is attempted. For example, J. Taffanel[12] placed the upper limit for sieved coal dust at about 2 oz/ft.^{3} while Allison[10] showed that the upper limit for Pittsburgh coal lay far in excess of the highest concentration employed, namely 0·973 oz/ft.^{3}. Hartmann, Jacobson and Williams[2] in their study of the effect of dust concentration on the maximum pressures and rates of pressure rise developed during coal dust

explosions found that a concentration of 2 oz/ft.^{3} of −200-mesh Pittsburgh coal dust dispersed in air produced a pressure of more than 70 lb./in.^{2}. Concentrations greater than 2 oz/ft.^{3} were not used but from the shape of the graph of maximum pressure and dust concentration given by these authors it would appear that the upper limit of zero pressure would be reached at a concentration well above this value. These authors also described preliminary experiments for the determination of the upper explosive limit of Pittsburgh coal dust (−200 Tyler sieve) in air. The pressures and rates of pressure rise are recorded together with the residual oxygen content of the explosion gases. With these experiments an upper limit of approximately 12 oz/ft.^{3} is indicated. Thus while undoubtedly an upper explosive limit does exist it is generally accepted as being ill defined. At high dust concentrations the curve relating maximum pressure and dust concentration approaches the zero pressure line so slowly that it is most difficult to determine the upper limit experimentally.

The composition of the dispersion medium

The most important variable is the oxygen concentration although other factors such as the nature of incombustible constituents other than oxygen, the inflammable gas content, the water vapour content, the temperature, pressure, specific heat and thermal conductivity of the dispersion medium also influence explosibility.

The limiting oxygen concentration

J. HARGER[13] claimed in 1912 that a reduction in oxygen concentration of 2 per cent below the lower explosion limit of oxygen concentration for a given coal dust will, in practice, definitely prevent explosion of the dust, and also that absolute guarantee against explosion from any coal dust, however finely divided, is obtained when the oxygen concentration is reduced to 17·5 per cent. Substantial confirmation of Harger's view was provided by H. H. BROWN and J. K. CLEMENT[14] at the U.S. Bureau of Mines where, using coil ignition and taking development of pressure as a criterion of ignition, the lower limit of oxygen concentration was found to be 16·8 per cent. Hartmann[9], however, has found that by using hot tube ignition with a tube temperature of 800 °C, coal dust clouds may be ignited in a medium containing only 10 per cent oxygen. This variation in the lower oxygen limit is probably explained by the very different energies of the igniting sources. Hartmann, Jacobson and Williams[2] have shown that whereas a cloud of Pittsburgh coal that will pass through a 200-mesh Tyler sieve cannot be ignited below 550 °C in a medium containing 50 per cent oxygen, a suspension of the same coal dust can be ignited in a medium containing 10 per cent oxygen if the temperature is increased to 750 °C.

It appears then that the lower oxygen limit for coal and other dusts is rather ill defined, probably because it is governed by the temperature, the thermal energy of the igniting source and also the state of division of the particles.

The effect of variation of oxygen content of the dispersion medium

Hartmann, Jacobson and Williams[2] observed that the maximum pressure and rates of pressure rise developed by the dusts of American coals, dispersed in air, increased with increasing dust concentration reaching maximum values and then decreased with further increase in dust concentration. When these coal dusts were dispersed in oxygen the pressure and rates of pressure rise obtained were much higher than those recorded in air for the same dust concentration. The values increased progressively with increased concentration to limits set by the strength of the explosion apparatus. For example, using a bituminous coal dust passed through a 200-mesh Tyler sieve, dispersed in air, the pressure developed increased from 35 lb./in.^{2} at a concentration of 0·2 oz/ft.^{3} to a maximum value of 90 lb./in.^{2} at a concentration of 0·9 oz/ft.^{3}. In oxygen, however, the corresponding pressures produced at these concentrations were 100 lb./in.^{2} and 230 lb./in.^{2}. These authors do not indicate whether the dust particles are burnt completely either in air or in oxygen. Assuming that the combustion is complete in each medium then the pressures developed in air and oxygen for a given dust concentration can only be correlated by assuming that appreciable heat loss by conduction and radiation occurs during the slower development of maximum pressure for explosion in air.

Hartmann and his colleagues showed also that for American coals increase in oxygen content of the dispersion medium reduces the minimum energy required for ignition, the minimum explosion concentration and the ignition temperature of dust clouds.

The effect of the moisture content of the coal dust

Hartmann, Jacobson and Williams[2] studied the effect of moisture on the exposibility characteristics of a Pittsburgh coal dust (−200-mesh Tyler) in air.

They found (*a*) little change in the lower explosion limit with increase in moisture content up to 8 per cent but that beyond this value the lower limit increased rapidly; (*b*) the minimum energy required for ignition is 50 to 60 mJ for moisture contents up to 5 per cent and this increases rapidly with further addition of moisture; (*c*) that at several dust concentrations there appeared to be an increase in explosion pressure and rates of pressure rise with increase in moisture content up to 5 per cent while further additions of moisture resulted in a fairly rapid decrease in pressure and pressure rates. Similar tests made with a sub-bituminous coal showed very little change in pressures and rates of pressure rise in the range 0 to 8 per cent moisture.

THE MECHANISM OF IGNITION OF COAL DUST CLOUDS BY ELECTRIC SPARKS, FLAMES AND HOT SURFACES

The mechanism of propagated combustion of suspensions of the dusts of many metals initiated by electric sparks, flames or hot surfaces must be limited to the exothermic gas–solid reaction producing the solid metal oxide, since the vapour pressure of the metal at the ignition temperature is

often so small that it cannot possibly play any part in the initiation and propagation of an explosion. For the explosion of clouds of coal dusts and the dusts of many other organic substances the mechanism may not be the same. If it is assumed that ignition is effected by purely thermal means then explosion may be due to either: (*a*) the solid–gas reaction between the coal particle and the oxygen of the dispersion medium, liberating sufficient heat to raise the temperature of the coal particles to a value at which they oxidize rapidly enough to give self-propagated oxidation throughout the dust cloud. This sudden heating of coal particles will, almost certainly for low rank coals, result in the evolution of volatile constituents which may then combine rapidly with oxygen to produce a luminous flame. The radiant heat emitted by these flame 'pockets' will probably provide additional preheat of the unburnt coal particles and thus increase the rate of propagation of combustion. Or (*b*) the partial decomposition by the ignition source of the coal particles in its immediate vicinity liberating inflammable gases which then combine rapidly with the oxygen present, producing more heat and so resulting in propagation of distillation and gaseous inflammation. The carbonized residues being heated to the flame temperature would be consumed rapidly in the presence of sufficient oxygen.

Theories of explosion mechanism

In 1875 M. VITAL[15] began a scientific investigation into the possibility of mine explosions being due solely to the combustion of dispersions of coal dust. This work led him to suggest that the explosion of a coal dust cloud was due to the coal particles being partly resolved by heat into gases which then formed an inflammable mixture with air. This gaseous mixture was then the medium for propagation of flame. From his observations Vital suggested that only coals possessing a sufficiently high volatile content would be inflamed. R. HOLZWART and E. VON MEYER[16] in 1891 studied the explosions of the dust clouds of brown coals using a stream of electric sparks as ignition source. They could not, however, find any relationship between the inflammability of the coal dusts and their volatile content.

In 1907 C. ENGLER[17] supplied further experimental evidence in support of the 'volatile theory' of ignition. He found that dusts which would evolve inflammable vapours on heating (coal, flour, naphthalene) could be ignited by electric sparks of sufficient intensity. Dusts of materials such as lamp black and wood charcoal which would not distil on heating could not be inflamed unless suspended in an atmosphere containing an inflammable gas (methane).

P. BEDSON and W. WIDDAS[18] at this time were studying the explosibility of a variety of organic dusts using coil ignition and measuring the pressures produced. It was observed that for a wide variety of dusts (starch, sugar, flour, coal *etc*) the higher the volatile content the more easily ignitable the dust cloud.

A number of workers have since confirmed the earlier observations on the increase of inflammability of bituminous coals with increase in volatile

content. A. L. GODBERT and R. V. WHEELER[19] determined the relative inflammabilities of some sixty British coals and observed that relative inflammability decreased in a general way with increase in rank. The reactivity to oxygen of the coals was then determined by measuring the volume of oxygen absorbed per hour by 100 g of the coal when heated to 100°C in air. When the relative inflammabilities were plotted against the reactivities practically all the points lay within a narrow well-defined band. These workers then suggested that relative inflammability increases with volatile content for the sole reason that volatile content is only an approximate measure of the degree of coalification and therefore chemical reactivity of the ulmin constituents of the coal. These authors found that the well-defined relationship between relative inflammability and reactivity is limited to bright coals only and that deviations can be expected when the dusts of durains are tested. This variation, they suggested, is due to the fact that the volatile constituents produced by the breakdown of the appreciable quantities of non-ulmin material present in durains are far more inflammable than the volatile products yielded by bright coals. The inference from this work appears to be that ignition results from the reactivity of the coal particles to oxygen, the heat liberated from the solid–gas reaction being propagated throughout the dust cloud. If the rate of heat evolution is high, as with a coal of high reactivity, a large percentage of inert dust is required in a mixture to suppress propagated combustion.

Many investigators including C. R. BROWN[20], H. E. NEWALL[21], Newall and F. S. SINNATT[22], R. A. SHERMAN, J. M. PILCHER and H. N. OSTBORG[23], S. W. PARR[24] and E. AUDIBERT[25], have determined the ignition temperatures of coal particles singly and in bulk. The ignition temperature is taken as the temperature at which the rate of heat evolution during oxidation of the particle surface exceeds the rate of dissipation of heat to the surroundings. In all tests on bituminous coals it is found that coals ignite at temperatures well below those at which any inflammable gas mixture may be distilled from the coals.

H. K. GRIFFIN, J. R. ADAMS and D. F. SMITH[26] in their study of the mechanism of combustion of individual particles of solid fuels, photographed the combustion at 1000°C of single coal particles in still air. From these observations they stated that the process of combustion could be separated into two stages: (*a*) the distillation and burning of volatile matter followed by (*b*) the burning of the residual carbon or coke which occupies 90 per cent of the time required to burn the whole particle.

D. J. PRICE and H. H. BROWN[27] on the other hand maintain that pre-distillation of gases from the solid particle is not a factor in the ignition of dust suspensions since the gases (if any) distilled from the easily ignitable dusts, at temperatures near the ignition points, are so high in their carbon dioxide and water vapour contents as to be non-inflammable.

More recently H. C. PORTER[28] has maintained that the ignition of suspended dust from solids in adequate surrounding air is a direct attack of oxygen on the solid surface of the particles. The work of G. B. TAYLOR, H. C. PORTER and E. C. WHITE[29] is quoted in which it is claimed that coal

dust suspensions in air could be inflamed without pre-distillation of any gas that could be a factor in the ignition.

E. JONES and A. G. WHITE[30] in their comparison of gas and dust explosions point out that, with few exceptions, the product of the net calorific value and the percentage of gas or vapour in lower limit gas–air mixtures is a constant for a large variety of inflammable gases and vapours with a value of about 450 cal/l. These authors consider that for gaseous mixtures propagation of flame occurs if the flame temperature reaches a certain critical value, which appears to be about 1400°C, and that increase in temperature above this value increases the flame speed. Despite the differences in ignition temperature of the various gaseous fuel–air mixtures the effective ignition temperature so far as propagation of flame is concerned seem to be much the same for all the gases and vapours considered.

Examination of the lower explosive limits of dust–air mixture reveals that in many instances the value is well below that of the gaseous limit mixtures (450 cal/l.). It might have been expected that since thorough mixing is more readily obtained with gases than with dust dispersions, the calorific value at the lower limit would be less for a gas–air than for a dust–air mixture. A limit mixture calorific value of 15 cal/l. is found for sulphur dust and values of 50 are fairly common. The authors use the data of L. J. TROSTEL and H. W. FREVERT[31] to show that the limit mixture calorific value of a Pittsburgh coal dust is 133 cal/l., *i.e.* well below the value for gaseous limit mixtures. The lower limit calorific value for sulphur dust means that the heat generated is barely sufficient to raise the mean temperature through 50°C whereas the ignition temperature of sulphur is about 260°C. It is evident then in this instance that flame propagation does not necessitate the raising of both dust and air to the ignition temperature of sulphur but that propagation occurs by virtue of local centres of burning particles, flame being propagated from one particle to another without apparently raising the main body of air to the temperature of the flame.

These authors then remark that the suggestion, made with reference to coal dust explosions, that the gaseous mixture formed by the distillation of the volatile constituents of the dust is the medium for the propagation of flame, cannot be generally true because the heat generated by the complete combustion of a coal dust is in many cases insufficient to maintain a gaseous phase inflammation. Moreover, this discrepancy between gas–air and coal dust–air lower limit calorific value seems to become more pronounced the greater the volatile content of the dust, thus although volatility evidently plays a part in dust explosions, inflammation cannot be attributed to the production of a homogeneous vapour–air mixture capable of propagating flame.

D. B. SPALDING[32] has derived equations which enable the combustion temperature and burning time of liquid fuel droplets and carbon particles to be determined. The assumption is made that during combustion all the oxygen available at the combustion surface is consumed immediately so that the rate-determining factor is the diffusion of gases through the gas film around each particle to and from the combustion surface. Assuming that

all the heat transfer is effected by conduction, Spalding shows that the burning time of a carbon particle, when dissociation is neglected, is thirteen times that of a kerosene droplet of the same diameter. The effect of dissociation of carbon dioxide on the combustion of carbon particles is shown to double the combustion rate. The reason given is that with dissociation the oxygen does not have to diffuse right up to the carbon surface, because the carbon monoxide formed by dissociation diffuses outwards to meet the oxygen when it is burnt to carbon dioxide. It is doubtful, however, whether the equation derived by Spalding can be applied to the explosion of coal dust clouds initiated by electric sparks in view of the following criticisms:

(*a*) The equations were derived on the assumption that thermodynamic equilibrium between the fuel surface and the oxygen molecules reacting was established immediately and that the combustion rate was determined by the rate of diffusion of oxygen to the fuel and the rate of diffusion of combustion products away from the fuel surface. With coals of high rank it is very probable that it is the rate of oxidation at the fuel surface which determines the rate of reaction and not the rate of diffusion of oxygen to the surface, while it is doubtful whether diffusion films of any appreciable thickness could exist in the turbulent conditions prevailing within a dust cloud formed by a blast of gas.

(*b*) The only mode of heat transfer considered by Spalding was that of conduction whereas in the combustion of carbon and coal particles, an appreciable amount of the heat liberated must be transferred by radiation from the burning particles.

R. H. ESSENHIGH[33] reviews the generally accepted mechanism of the complete combustion of carbon as being a two-stage reaction in which the following processes occur:

(*1*) The primary reaction is a heterogeneous surface reaction forming the oxides of carbon in a specific ratio and which itself involves the following steps: (*a*) transport of oxygen to the solid surface by diffusion; (*b*) bombardment of the solid surface and adsorption of oxygen to form an oxide film; (*c*) desorption of the oxygen which carries with it atoms of carbon in combination as carbon monoxide or carbon dioxide; (*d*) transport of reaction products away from the solid surface (with further oxidation of carbon monoxide).

(*2*) The secondary reaction is a homogeneous gas phase reaction between carbon monoxide and excess oxygen. Essenhigh refers to experimental work carried out in the 1920's in which it was shown that during the oxidation of carbon at elevated temperatures a critical temperature was reached at which the temperature coefficient of the reaction suddenly changed. This critical temperature has hitherto been assumed to indicate a change in the rate-controlling step from that of chemical reaction at temperatures up to the critical value to that of physical diffusion at temperatures above the critical. The author cites the experimental results of various workers on the combustion of carbon which show that at temperatures below the critical value the rate of reaction is practically independent

of oxygen concentration and that the reaction temperatures coefficient indicates an activation energy of approximately 30000 cal/mole. At temperatures above the critical (approximately 1000°C) the reaction rate becomes dependent on oxygen concentration and the reaction temperature coefficient now gives an activation energy value of only 4000 cal/mole.

Essenhigh suggests that steps *a* and *d* of the primary reaction, *i.e.* the diffusion process, need not be the rate-limiting factor at temperatures above the critical but that the change in the temperature coefficient at the critical temperature may be adequately explained by a change in the rate-limiting reaction from step *c* to step *b* of the primary reaction.

At temperatures below the critical value it is considered that the rate of adsorption of oxygen is rapid in comparison with the rate of desorption which requires a high activation energy. The rate of desorption is then the rate-controlling reaction and would be expected to be independent of oxygen concentration. At the critical temperature the reaction temperature coefficient changes suddenly, giving an activation energy value of 4000 cal/mole which is indicative of adsorption rather than desorption. This must mean that the rate of desorption has increased suddenly so that vacant sites have been formed on the carbon surface and that the reaction rate will now be dependent on the rate of adsorption and will therefore be influenced by oxygen concentration.

From their study of the effect of coal concentration on the ignition times of pulverized coal clouds when injected into a small furnace held at various temperatures, B. GHOSH and A. A. ORNING[34] concluded that the unburnt coal particles receive only a part of their heat from the furnace and that an appreciable portion is transferred by radiation from the flame front. These authors suggest that (*a*) the ignition process of pulverized coal clouds involves heat transfer to the coal particles by radiation and heat loss by conduction into the surrounding atmosphere and that anything which changes the rate of these processes will change the rate of flame propagation. Because radiant heat transfer through transparent media depends upon angle factors, but not upon distance, the propagation of a pulverized coal flame depends upon the size and geometry of the flame as well as upon the fuel distribution and the aerodynamic pattern. (*b*) As the propagation of a pulverized fuel flame depends on the flow of radiant energy throughout the flame it is distinct from gaseous flames in so far as fuel gases are transparent to thermal radiation, and flame propagation then depends upon energy transfer from zones within or immediately adjacent to that portion of the flame front under consideration.

H. C. HOTTEL and I. McC. STEWART[35] give the following general mechanism for the combustion of particles of pulverized coal. The combustion process may be divided into three successive periods—ignition, distillation and combustion of volatile matter and finally combustion of fixed carbon. During the ignition period each particle absorbs heat from the furnace chamber and from previously ignited fuel particles. Moisture is driven off and, as the temperature rises, carbon dioxide and some hydrocarbons are evolved until the ignition temperature is reached. The tempera-

ture now rises rapidly until the heat loss by radiation balances the liberation of heat by combustion. The initial rate of rise of temperature will depend on the temperature of the flame and of the surroundings, the specific surface of the particle, the temperature and quantity of air surrounding the coal, the convective heat transfer coefficient, the thermal diffusivity of the coal and the density of the cloud of pulverized coal. The temperature necessary for ignition also varies with these conditions but it is somewhere in the range 200° to 300°C for lignite and 450° to 600°C for anthracite and increases with increase in the rank of the coal. When the heat required to bring the coal to ignition temperature (high for anthracite) is added to that required for removal of moisture (highest for lignite) the total heat requirement for ignition is found to be lowest for bituminous coal. A further factor contributing to the relative ease of ignition of the middle rank coals is the high rate of combustion of the volatile matter of an adjoining portion of the fuel cloud which has reached ignition temperature and is burning.

It is difficult to correlate the results of investigations into the combustion of coal particles in pulverized fuel firing with those obtained from a study of explosions of coal dust cloud initiated by electric sparks. In pulverized coal firing the preheat of the unburnt particles by the heat radiated from the furnace and burning particles is large enough to heat the particle to its ignition temperature at a rate which is practically independent of the reactivity of the coal used. With spark-initiated dust explosions the thermal energy of the igniting source is so small that initiation and propagation of explosion must be influenced considerably by the reactivity of the coal particles.

EXPERIMENTAL PROCEDURE

A modified form of the apparatus developed by Hartmann[3] in his study of the fire hazard associated with finely divided metal dusts has been used to determine the explosibility characteristics of a range of South Wales coals and selected English coals. The explosibility characteristics measured include: (*a*) the relative minimum explosive concentration of coal dusts which may be defined as the lowest concentration of dust in a given dispersion medium which will produce explosive rates of inflammation when ignited by an electric spark; and (*b*) the maximum pressure together with the average and maximum rates of pressure increase developed during explosion when known quantities of sized fractions of the dusts of various coals were dispersed in air or other media of known oxygen content and ignited by an electric spark.

Relative minimum explosive concentration apparatus

The explosion chamber (*Figure 1*) consisted of a *Perspex* cylinder 12 in. long, $2\frac{3}{4}$ in. internal diameter with a wall thickness of $\frac{1}{4}$ in. Along the length of the cylinder at 2 in. intervals holes were drilled through which electrodes could be inserted and which might be sealed, when not in use, with *Perspex* plugs. The bottom of the cylinder was closed by a polished brass cup *E* in which the coal dust was placed. The top of the tube was

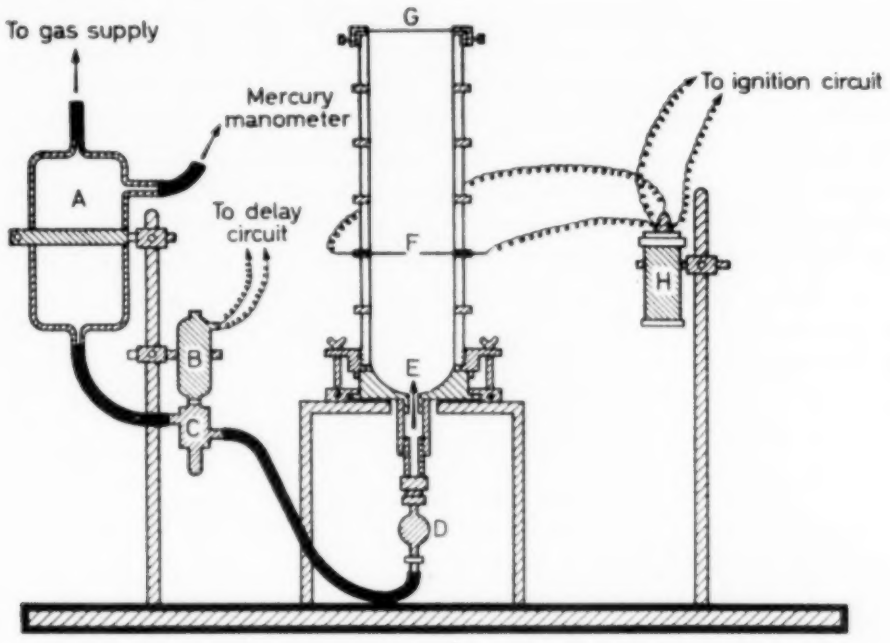

Figure 1. Diagram of apparatus used to determine the relative minimum explosive concentration of coal dusts

closed by a paper diaphragm *G* of approximately 3 lb./in.² bursting strength, the paper being held firmly in position by a brass clamping ring. The electrodes *F*, shown in the second position, were of 18 s.w.g. tungsten wire. The reservoir *A* was charged with the dispersion medium to a pressure which was registered by a mercury manometer. Dispersion gas was admitted to the cylinder by way of the valve *C* which was operated electrically by the solenoid *B* and then through the non-return valve *D*. The gas entering

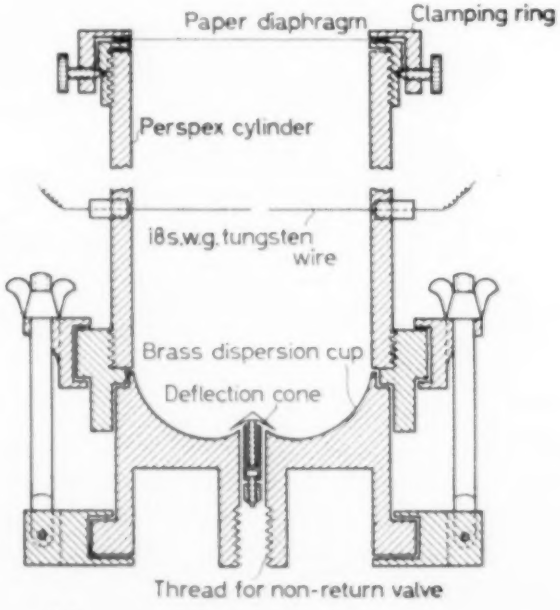

Figure 2. A detailed sectional diagram of the Perspex *explosion cylinder assembly*

the cylinder is forced downwards by a deflection cone on to the dust in the brass cup *E* and carries the dust with it up to the polished sides of the cup and into the *Perspex* cylinder. A more detailed drawing of the explosion tube and dispersion mechanism is shown in *Figure 2*.

The coal dust dispersion is ignited by the inductive spark produced across the electrodes *F* by the high voltage induced in the secondary winding of the ignition coil *H* when a condenser charged to approximately 200 V is allowed to discharge through the primary winding. To ensure correct synchroni-

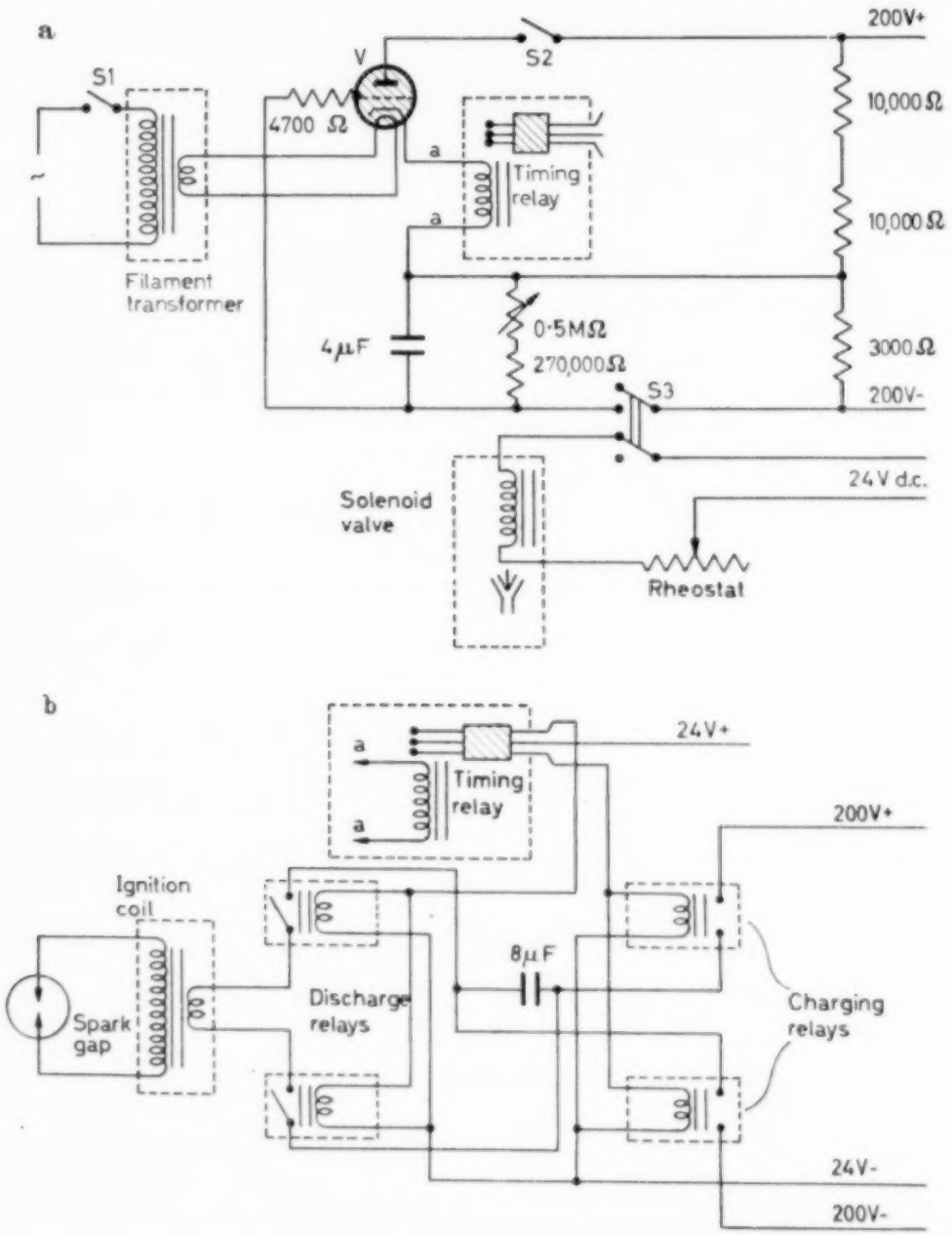

Figure 3. Circuit diagrams of the delay and ignition apparatus used in the determination of relative minimum explosive concentrations

zation between the single spark discharge and the formation of the dust cloud, a variable delay system illustrated in *Figure 3a* was developed. The valve V, an argon-filled triode, carries the operating coil of a timing relay as part of its cathode load. With the ganged switch S_3 in its normal position, *i.e.* the solenoid valve circuit broken, the cathode is held at a potential of approximately 30 V positive with respect to the grid. This bias, supplied from the 23000 Ω potentiometer, ensures that the valve does not conduct. Operation of the switch S_3 opens the solenoid-controlled valve admitting the dispersion medium to the explosion tube while the return from the grid to the 200 V negative is broken. The source of the bias voltage is thus removed, but the valve will not conduct until the 4 μF condenser, which is charged to the bias voltage, has discharged sufficiently. Variation of the resistance of the condenser discharge path will therefore vary the delay between the operation of S_3 and the operation of the timing relay.

The circuit used for the production of a spark across the electrodes is shown in *Figure 3b*. Operation of the timing relay in the valve cathode circuit allows an 8 μF condenser, already charged to 200 V, to discharge through the primary winding of an ignition coil. The high voltage induced in the secondary winding of the coil produces a spark discharge across the electrodes which are positioned inside the *Perspex* explosion tube.

Test procedure

With the low dispersion gas pressure used (15 cm mercury) coal particles larger than 200 B.S. sieve size could not be dispersed satisfactorily. Accordingly, the coal samples were ground until the whole of the sample passed through a 300 B.S. sieve before the test. The effect of non-uniform distribution of the coal dust in the cloud may be minimized by determining the limiting explosive dust concentration for each of the five electrode positions and obtaining a mean value for the limiting concentration. However, only one electrode position has been used and non-uniform distribution is accepted as being an inherent feature of the apparatus. The standardization of the method and conditions of dust dispersal does, however, ensure that the distribution of the dust, though not uniform, is reasonably constant for all tests so that relative values of minimum explosive concentration may be obtained.

Air-dispersed clouds of the range of coals investigated could not be ignited by the single spark discharge but explosions could be obtained with dispersion media containing 25 per cent oxygen. The effect of oxygen concentration in the dispersion medium on the limiting dust concentration was studied by using dispersion media containing 25, 55 and 100 per cent oxygen.

Results

The effect of coal rank and oxygen content of the dispersion medium on the relative minimum explosive concentration is shown in *Figure 4*. The spark gap used was 0·072 in., the minimum concentration being taken as the lowest coal-dust concentration for which inflammation accompanied by rupture of the paper diaphragm occurred.

The variation of limit concentrations of coal dust with rank is quite definite, maximum variation occurring with coals of less than 25 per cent volatile matter (d.a.f.) using dispersion media containing 55 and 100 per cent oxygen.

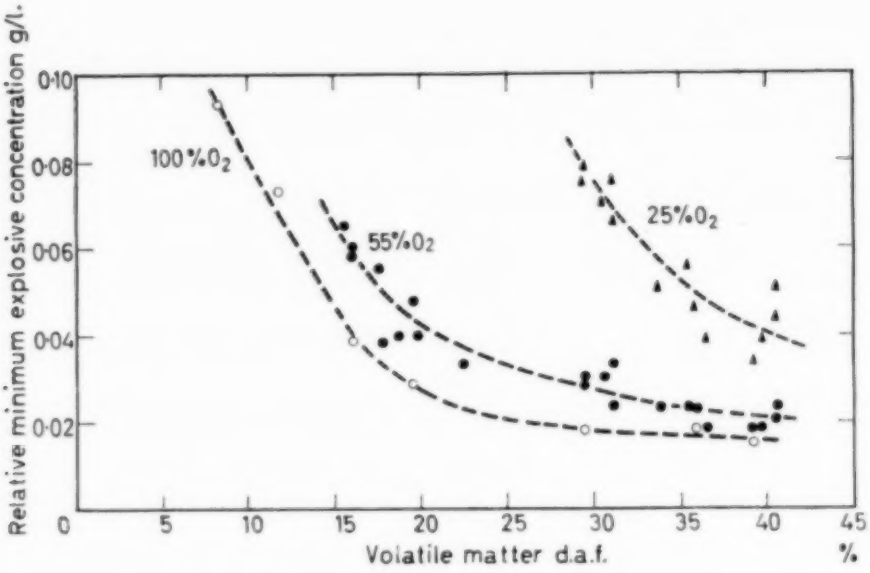

Figure 4. Variation of the relative minimum explosive concentration of the −300 B.S.S. coal fractions with rank using dispersion media containing 25, 55 and 100 per cent oxygen

The effect of oxygen concentration is most marked in the change of oxygen concentration from 55 to 25 per cent, a number of the coals being non-inflammable at the lower oxygen value.

Measurement of the maximum pressures, the average and the maximum rates of pressure increase developed during dust explosions

Apparatus

For the quantitative measurement of the maximum pressure and rates of pressure increase during dust explosion the apparatus used for the determination of limiting explosive concentration is modified. The *Perspex* cylinder is replaced by a chromium-plated mild steel cylinder of identical size and shape, screw threaded at each end and drilled in the same positions for electrode insertion. A steel adaptor connects the steel explosion tube to an optical manometer which is similar in design to the U.S. Bureau of Mines instrument. The optical manometer illustrated diagrammatically in *Figure 5* consists of a rectangular mild steel box *H* into which is welded the steel tube carrying the lamp assembly *J*. The open upper end of *H* is slotted to take the photographic drum outer cylinder *I*. The drum carrying the photographic film is fitted inside the lightproof outer cylinder *I* and is rotated at constant speed by the electric motor *K* using a high reduction worm drive. A polished steel concave mirror hinged at its focal centre is fitted inside the base of the manometer tube at *G* so that the pencil of light

emerging from *J* is reflected vertically upwards and brought to a focus at the surface of the moving film.

The top of the explosion vessel is sealed at *F* by a stainless steel diaphragm. Movement of the centre of the diaphragm is transmitted by way of a light rod to the mirror which deflects the light beam and so produces an optical magnification of the diaphragm movement.

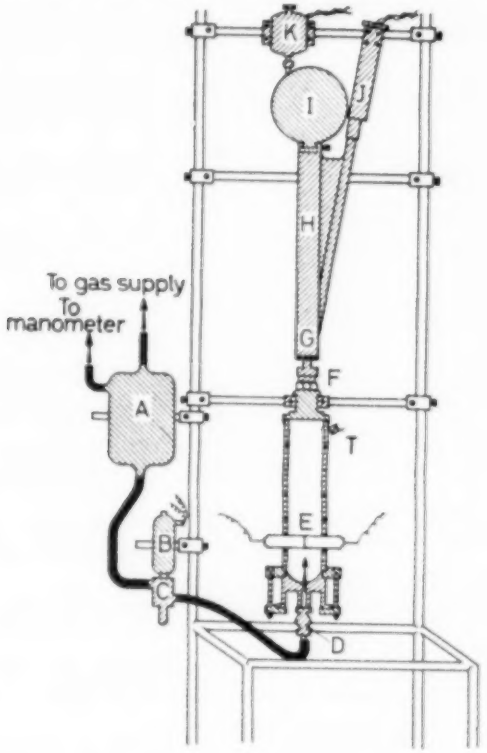

Figure 5. Apparatus used for the measurement of the maximum pressures and rates of pressure increase developed during coal dust explosions

In order to extend the range of coals which could be exploded in a given dispersion medium the apparatus producing a single synchronized spark was replaced by the high energy continuous spark generator illustrated diagrammatically in *Figure 6*. The ganged switch *S* enables the solenoid

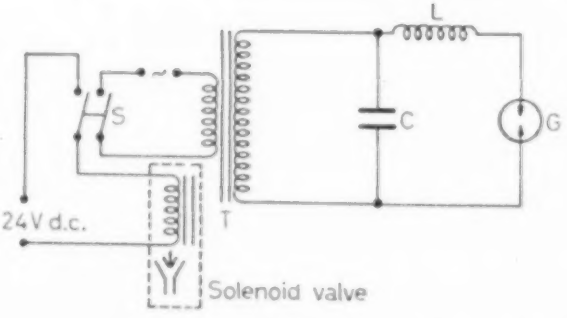

Figure 6. Circuit diagram of apparatus used to produce continuous high voltage high energy sparks

valve admitting the dispersion medium to be operated when the high voltage transformer *T* is energized. The 8 kV output from the transformer is applied across a 0·0005 μF condenser *C* and on to the gap electrodes through a 0·5 mH inductance *L*.

Procedure

Before each test the explosion tube is flushed slowly with the dispersion gas until all the air has been displaced. A reservoir pressure of 15 in. mercury is again used to disperse known weights of − 300 B.S.S. fractions of the coal dusts upwards into the explosion tube. Having previously calibrated the manometer against statically applied hydraulic pressures and measuring the speed of the moving film, the pressure–time records obtained were then used to determine (*a*) the maximum pressure developed (lb./in.^{2}); (*b*) the average rate of pressure rise during the period between ignition and the attainment of maximum pressure (lb./in.^{2}/sec); (*c*) the maximum rate of pressure rise given by the gradient of the steepest position of the pressure–time trace (lb./in.^{2}/sec). Between each test the explosion tube is cleaned thoroughly and the electrode gap reset.

Results

(*1*) *Variation of coal dust explosibility with rank*—In order to obtain the ignition of as many coals as possible, oxygen was used as the dispersion medium 0·15 g of the − 300 B.S.S. coal dust fraction being used in each test. The coal dust cloud was ignited from the lowest pair of electrodes in each instance. The variation of explosibility illustrated graphically in *Figure 7*,

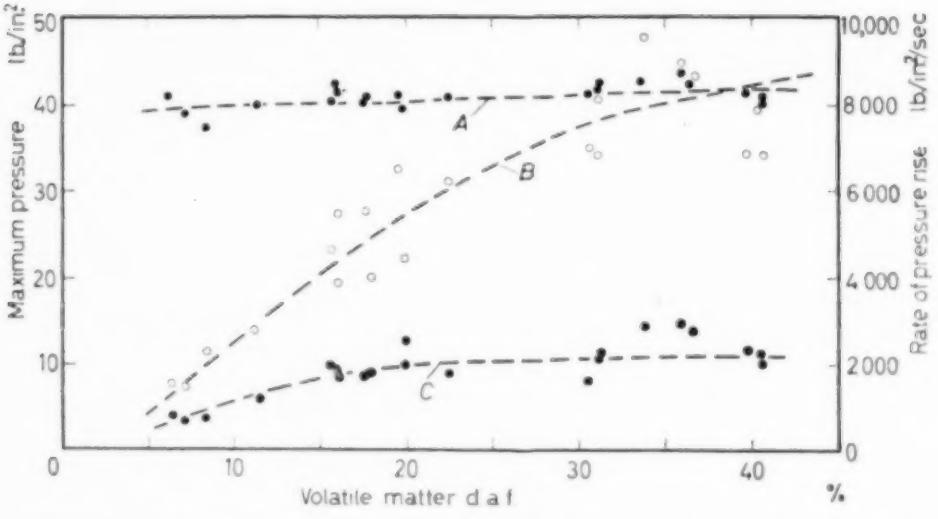

Figure 7. The variation of coal dust explosibility characteristics with rank using oxygen dispersion. A *maximum pressure;* B *the maximum and* C *the average rate of pressure increase*

shows that the dusts of a wide range of coals can be ignited in oxygen by electric sparks and that (*a*) there is little if any variation of the maximum pressure developed during the explosion of coal, ranging from anthracite to gas coals, when dispersed in oxygen, suggesting that the distribution of coal particles in the dust cloud, if not uniform, is reasonably constant for each test; (*b*) there is a definite increase in the average rate of pressure rise with decrease in rank to coals of 20 per cent volatile matter (d.a.f.), but that for further decrease in rank the increase in the average rate is small; (*c*) the

maximum rate of pressure rise increases rapidly and continuously with decrease in rank from anthracite to gas coals, the greatest variation being shown by coals of less than 20 per cent volatile matter (d.a.f.).

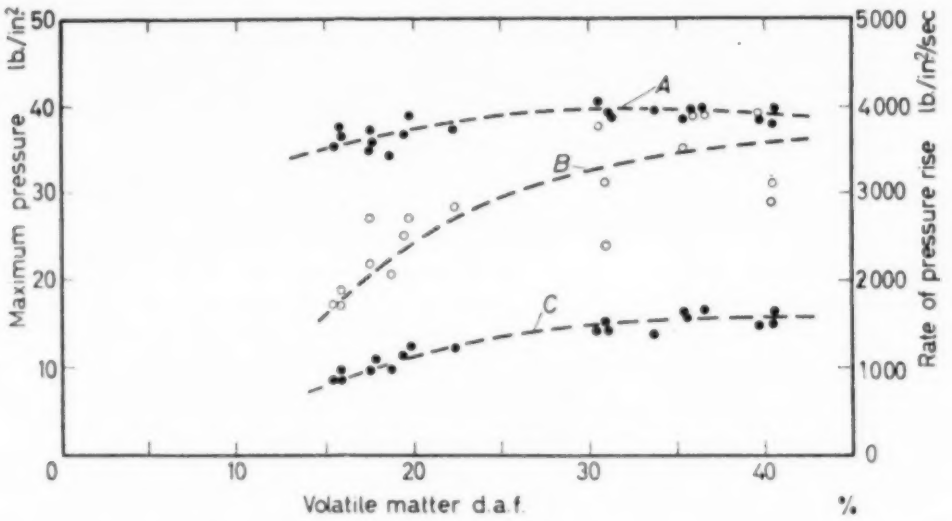

Figure 8. The variation of coal dust explosibility characteristics with rank using a dispersion medium containing 55 per cent oxygen. A maximum pressure; B the maximum and C the average rate of pressure increase

(2) *Effect of variation of the oxygen content of the dispersion medium on the explosibility of coal dusts—Figure 8* illustrates the variation of coal dust explosibility characteristics with rank using as dispersion gas an oxygen–nitrogen mixture containing 55 per cent oxygen 0·15 g of −300 B.S.S. coal dust fraction being used in each test. It can be seen that the coals of volatile content 15 per cent and below cannot be ignited by electric sparks in this medium and that both the maximum pressures and the average rates of pressure increase now show a definite increase with decrease in rank over the range 15 to 30 per cent volatile matter. The maximum rates of pressure rise also show their greatest variation with rank over this range. In

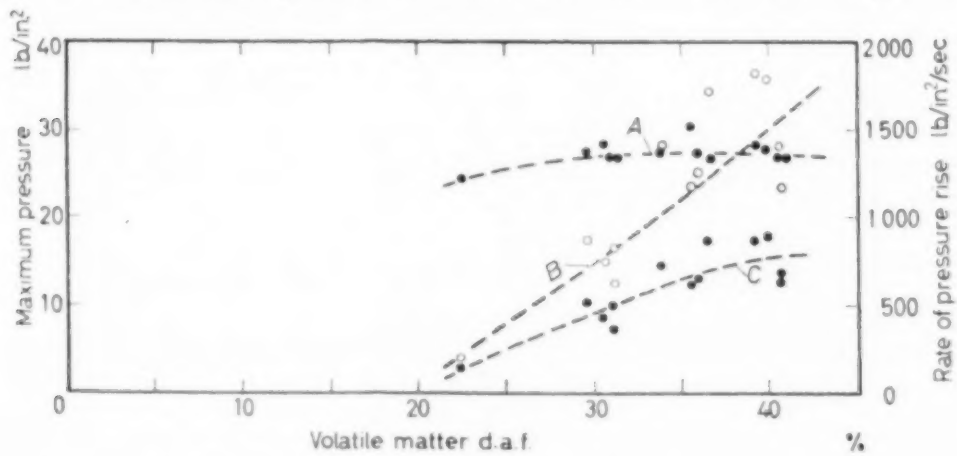

Figure 9. The variation of coal dust explosibility characteristics with rank using a dispersion medium containing 25 per cent oxygen

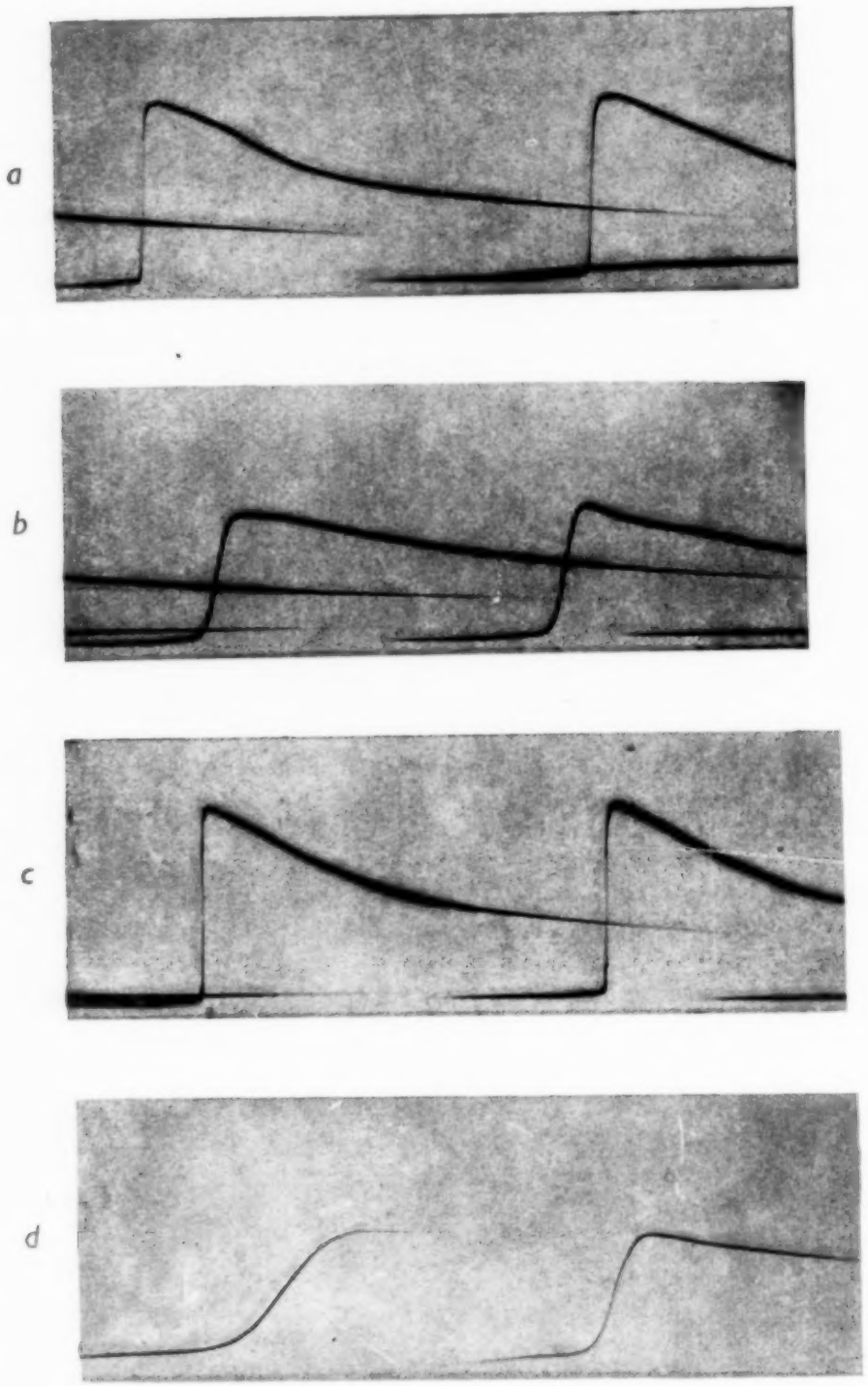

Figure 10. Explosion records produced by 0·15 g quantities of the −300 B.S.S. fraction of a coal dispersed in: a *55 per cent oxygen;* b *25 per cent oxygen;* c *100 per cent oxygen; and* d *air*

addition, the maximum rates of even the low rank coals have been decreased considerably by the reduction in oxygen concentration from 100 to 55 per cent. The effect of a further reduction of oxygen concentration to 25 per cent is shown in *Figure 9*. Here all the coals of less than 22 per cent volatile content are unreactive while all three of the explosibility characteristics have been reduced appreciably by the further reduction in oxygen content. Both the maximum and average rates of pressure increase now increase rapidly and continuously with decrease in rank while the maximum pressure developed remains reasonably constant for coals of more than 30 per cent volatile matter. The fact that the maximum pressures are much lower in 25 per cent oxygen, even though the quantity and particle size of the dust fraction has remained constant, suggests that combustion is incomplete. This is confirmed by the observation of small quantities of combustible dust in the brass dispersion cup and on the explosion tube surface near the electrodes after explosions in the 25 per cent oxygen mixture.

The use of air as dispersion medium using test quantities of 0·15 g of −300 B.S.S. coal fractions restricted the number of ignitable dusts to those containing more than 33 per cent volatile matter (d.a.f.). The maximum pressures obtained were the same as those obtained in the 25 per cent oxygen but the average and maximum rates of pressure were still further reduced.

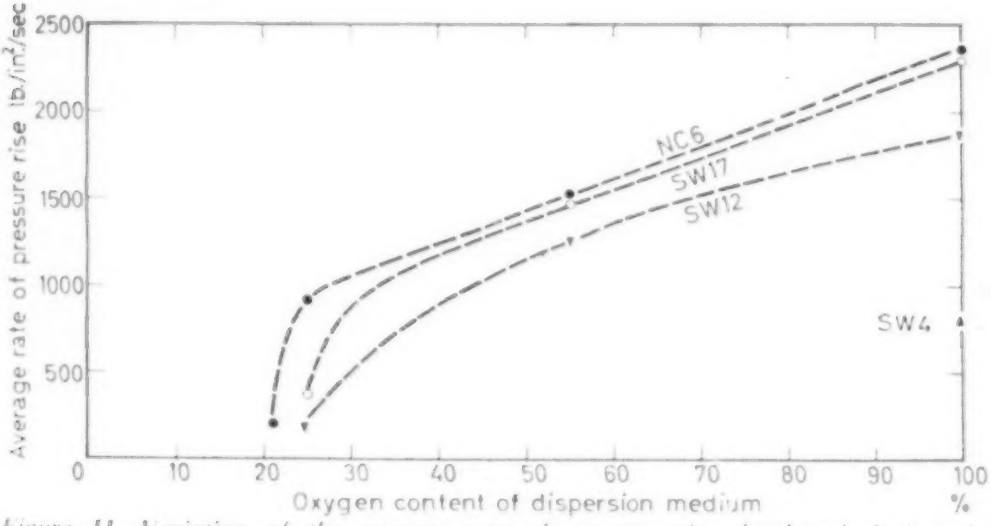

Figure 11. Variation of the average rate of pressure rise developed during the explosion of the dusts of four coals with the oxygen content of the dispersion medium. Volatile contents (d.a.f.): NC6, 39·7 per cent; SW17, 31·2 per cent; SW12, 22·3 per cent; SW4, 8·3 per cent

Typical pressure–time records obtained in each of the dispersion media used are shown in *Figure 10*. The average rates of pressure rise developed using 0·15 g sample of the 300 B.S.S. fraction of four coals, which are representative of the range of coals studied, are plotted against the oxygen content of the dispersion medium in *Figure 11*. For the three coal samples with more than 20 per cent volatile matter the average rate of pressure increase is directly proportional to the oxygen particle pressure for oxygen contents of more than about 40 per cent. Using dispersion media containing

less oxygen, the average rate of pressure increase of the highest rank coal decreases most rapidly while that of the lowest rank remains directly proportional to the oxygen partial pressure down to an oxygen concentration of 25 per cent.

(3) *The effect of dust concentration on the explosibility of coal dusts*— Quantities of the −300 B.S.S. fractions of the dust of a high volatile coal ranging from 0·05 to 0·20 g were exploded in oxygen. Quantities of the same coal dust ranging from 0·15 to 0·45 g were then exploded in a medium containing 25 per cent oxygen as weights less than 0·15 g could not be ignited in this medium.

The variation of the explosibility characteristics with dust concentration from each of the two dispersion media is shown graphically in *Figure 12*. There is a rapid increase in all three of the explosion characteristics with

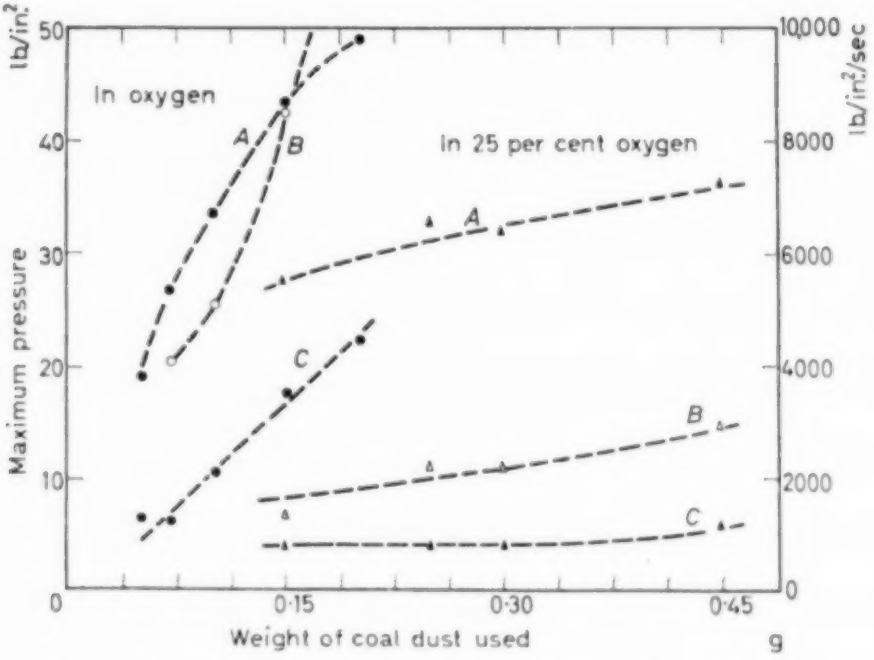

Figure 12. The effect of coal dust concentration on explosibility charateristics using oxygen and a mixture containing 25 per cent oxygen as dispersions media. maximum pressure; B the maximum and C the average rate of pressure increase

increase in dust concentration for the explosions in oxygen. For explosions in the 25 per cent oxygen mixture the increase of maximum pressure, average and maximum rates of pressure rise with increase in dust concentration is small.

Comparison of the observed with the theoretical maximum pressures developed during explosion

The completeness of combustion during the explosion of a coal dust of known ultimate analysis is first assessed by analysing the residual explosion gases and measuring the total quantity of carbon dioxide produced during explosion. The net calorific value of the coal is then used to determine the

heat liberated during the formation of the explosion products found by analysis. The flame temperature calculated, assuming that the whole of the explosion gases, excess oxygen and diluent gas are raised to the flame temperature and that heat loss by radiation and conduction is negligible, would result in a pressure increase of approximately 95 lb./in.^{2} for the explosion of 0·15 g of the coal. The pressure increase recorded during the explosion of 0·15 g of the coal was 40·0 lb./in.^{2}, *i.e.* less than half the calculated value.

THE CORRELATION OF THE OBSERVED WITH THE CALCULATED MAXIMUM PRESSURES

Incomplete combustion

Combustion may not be complete at the moment the maximum pressure is obtained. The analysis of the explosion gases is carried out some minutes after the maximum pressure is reached. The calculated heat evolution during the explosion may not all have been released when the peak pressure is reached and it is possible that burning of both solid and gaseous combustibles may still be proceeding at a slower rate after the development of maximum pressure. The flattened peaks followed by the very gradual decrease in pressure recorded on the pressure–time records of several of the explosions certainly seem to indicate that the combustion is not complete when the peak pressure is recorded.

If, owing to the size of the coal dust fraction, the particles have not been consumed completely when the peak explosion pressure is reached, then further reduction in the particle size should result in the development of higher pressures and increased rates of pressure rise. Accordingly small quantities of the −300 B.S.S. coal fraction were ground by hand in an agate mortar for an hour. A high volatile coal dust was tested several times using both the normal −300 B.S.S. and the finely ground dust. The results achieved from the explosions of 0·15 g of the coal in oxygen are given in *Table 1* while the pressure–time records are shown in *Figure 13*. *Table 1* shows that the reduction in particle size has resulted in an increase in the maximum pressure developed together with the average and maximum rates of pressure increase. The rate of decay of pressure after the peak value is seen to be much greater for the explosions of the finely ground dust than for those of the −300 B.S.S. fractions. This indicates fairly

Table 1

Pressure lb./in.^{2}		*Rate of pressure increase lb./in.^{2}/sec*			
Maximum	*Mean value*	*Average*	*Mean value*	*Maximum*	*Mean value*
300 B.S.S.					
40·5		2910		5800	
40·0	40·4	2880	2800	5800	5950
40·5		2910		5570	
40·5		2500		6650	
Finely ground dust					
46·0		5510		7500	
42·5	44·3	4170	4575	6650	7280
45·5		4910		7500	
43·0		3710		7500	

conclusively that further reduction in particle size results in a more rapid combustion and so reduces the quantity of heat liberated after the peak pressure has been reached.

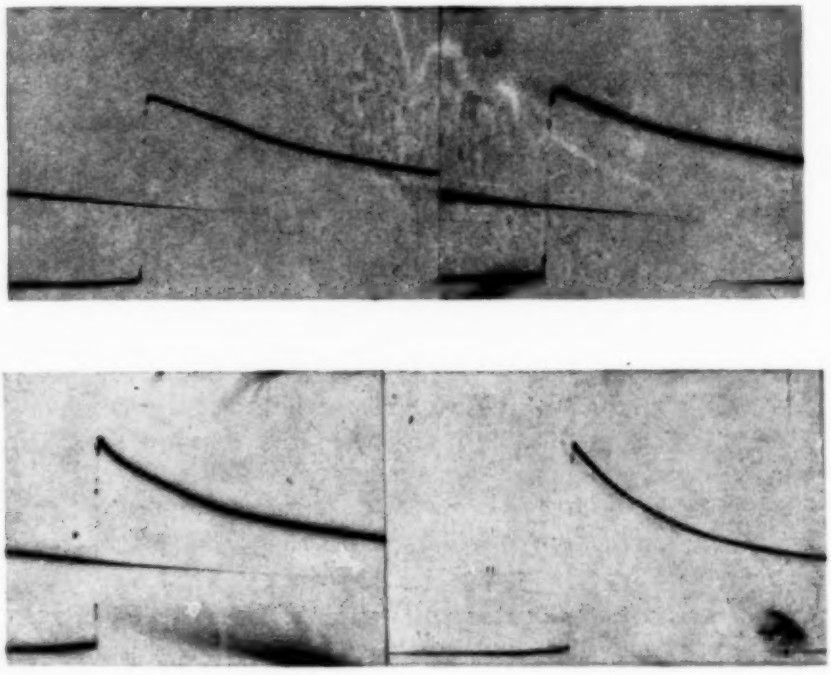

Figure 13. Explosion records illustrating the effect of prolonged grinding on the shape of the pressure time traces: a—300 B.S.S. fraction; b finely ground dust

Heat losses by radiation and conduction

Referring to *Figure 7* it can be seen that increase in coal volatile content from 6·5 to 17·6 per cent is accompanied by a 50 per cent decrease in the duration of explosion. The maximum pressures developed by these two coals are, however, practically equal. If appreciable quantities of heat are lost during explosion by radiation and conduction then the doubling of the explosion rate should result in a considerable reduction in heat loss, thus allowing higher pressures to be recorded. The fact that this effect is not observed suggests that radiation and conduction losses are not responsible for any appreciable loss of pressure. Practical evidence of this was obtained by inserting a highly polished aluminium sleeve inside the explosion cylinder so that any radiant heat loss should now be reduced considerably by virtue of the reflecting properties of the polished sleeve. Repeated tests with the dusts of several coals showed that after allowance for the slight reduction in internal volume of the explosion tube the pressures obtained with and without the sleeve were practically equal while the rates of pressure rise were increased slightly by the modification.

Distribution of the coal dust within the cloud

Change of electrode position from the lowest to the central position resulted in a marked decrease in both the average and maximum rates of pressure

increase. If the dust is distributed uniformly throughout the cloud then ignition at the central electrodes should give rates of pressure rise higher than those obtained from explosions initiated from the lowest electrode position. Ignition at the central electrodes of a uniformly distributed dust cloud would result in flame spreading in both directions and give as a result a much higher rate of pressure development than the almost unidirectional flame produced after firing from the lowest electrode positions. The fact that the reverse effect is obtained indicates that the dust dispersion is by no means uniform, the dust being concentrated in the lower half of the explosion tube.

With non-uniform distribution of dust it is most unlikely that all the gases in the upper part of the explosion tube are heated to the flame temperature so that the average gas temperature in the explosion tube will be less than that of the flame and could account for at least part of the difference between the observed and calculated maximum pressures.

The mechanism of the propagation of an explosion wave in coal dust clouds

Considerable doubt still exists as to whether the predistillation or volatile theory gives a more satisfactory explanation of the explosion propagation in a coal dust cloud than the theory that propagation is effected by the radiant heat emitted from the gas–solid reaction. Further experiments were therefore conducted in an attempt to elucidate the explosion mechanism.

The explosibility of dispersions of coal–inert dust mixtures

Quantities of up to 0·6 g of the −200 B.S.S. fraction of incinerated Fuller's earth were added to and mixed thoroughly with 0·15 g of the −300 B.S.S.

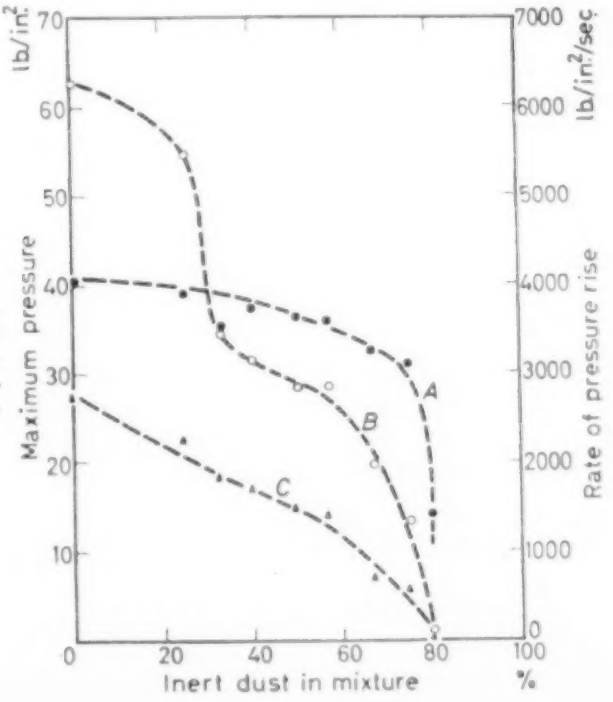

Figure 14. The effect of the addition of inert dust on the explosibility characteristics of coal dust. A maximum pressure; B the maximum and C the average rate of pressure increase

fraction of a high volatile coal. The mixtures were exploded in oxygen using the lowest electrode position. The variation of the explosibility characteristics with quantity of inert dust added is shown in *Figure 14*. The addition of the inert dust decreases, almost linearly, both the maximum pressure developed and the average rate of pressure rise up to an inert dust content of 60 per cent. Further additions of inert dust increases progressively the rate of decrease of these characteristics and suggests that zero explosibility would be reached with an inert dust content of 85 per cent. The maximum rate of pressure rise decreases sharply for inert dust contents up to 35 per cent after which the decrease is gradual up to 60 per cent inert dust, beyond which the maximum rate decreases rapidly to zero.

The effect of the blending of high and low rank coals on explosibility

All attempts to ignite dispersions of the −300 B.S.S. fraction of a coal of 5·3 per cent volatile matter (d.a.f.) in oxygen were unsuccessful for quantities of dust up to 0·5 g. It was found that this coal could be ignited if small quantities of a high volatile coal were blended with it. Accordingly 0·01 g of a high volatile coal (−300 B.S.S. fraction), a weight which was insufficient to give an explosion when used alone, was blended with 0·15 g of the non-explosive anthracite and the mixture dispersed and tested in oxygen. Positive results were obtained in each instance and the explosibility characteristics recorded are shown in *Table 2*. The explosibility characteristics of the high rank coals which could be exploded in oxygen without blending are shown in *Table 3*.

Table 2. Explosions in oxygen of coal dust blends

Weight of coal dust g		*Maximum pressure lb./in.²*	*Rate of pressure rise lb./in.²*	
Coal 1 V.M. (d.a.f.) = 5·3	*Coal 2 V.M. (d.a.f.) = 39·7*		*Average*	*Maximum*
0·15	0·01	40·0	410	630
0·15	0·01	39·5	450	820
0·15	0·01	40·5	510	890
—	0·01	*No pressure increase*		
0·15	—			

A comparison of *Tables 2* and *3* reveals that the rates of pressure rise during the explosion of 0·15 g of the anthracite blended with 0·01 g of a low rank coal are essentially those of an anthracite and are lower than those obtained with a coal of 6·4 per cent volatile matter (d.a.f.) which could be ignited in oxygen without blending. The 0·01 g of the low rank coal has

Table 3. Explosions of 0·15 g quantities of −300 B.S.S. coal fractions in oxygen

Coal	*V.M. (d.a.f.) per cent*	*Maximum pressure lb./in.²*	*Rate of pressure rise lb./in.²*	
			Average	*Maximum*
3	6·4	41·0	870	1600
4	7·1	39·0	700	1570
5	8·3	37·5	800	2350
6	11·4	40·0	1270	2830

therefore acted merely as a source of heat to initiate and assist propagated combustion of the anthracite and does not influence the explosion characteristics which remain those of a high rank coal.

The effect of low temperature atmospheric oxidation of coal on its explosibility

If the reaction responsible for the initial evolution of heat during a coal explosion is that between the solid particle surface and gaseous oxygen then pre-oxidation of the coal particles before explosion should result in a decrease in explosibility. Accordingly, small quantities of the −300 B.S.S. fractions of a coal of 39·2 per cent volatile matter were spread on glass trays in the layers and allowed to remain in an air oven at a temperature of 105°C for a period of 100 hours. Both the oxidized and fresh dust samples were then allowed to remain exposed to the atmosphere at room temperature for two days so that their moisture contents would be comparable. Each sample was then tested several times and the explosibility characteristics obtained in oxygen and in 25 per cent oxygen mixtures are shown in *Table 4*. The results obtained for oxygen dispersion indicate a definite decrease in the rates of pressure development after oxidation. Tests in the oxygen–nitrogen mixture, however, show little change in explosibility after oxidation.

Table 4. Effect of atmospheric pre-oxidation at 105°C on explosibility of 0·15 g of a coal of 39·2 per cent volatile matter (d.a.f.)

Dispersion medium	*State*	*Maximum pressure lb./in.²*	*Rate of pressure rise lb./in.²/sec*	
			Average	*Maximum*
Oxygen	*Unoxidized*	42·5	2620	5800
Oxygen	*Unoxidized*	41·5	2560	4980
Oxygen	*Oxidized*	40·5	1590	3000
Oxygen	*Oxidized*	44·5	2130	4150
25 per cent Oxygen mixture	*Unoxidized*	27·5	790	1990
Oxygen mixture	*Unoxidized*	29·0	960	1660
Oxygen mixture	*Oxidized*	27·5	910	2150
Oxygen mixture	*Oxidized*	28·0	930	1690

Fresh quantities of the −300 B.S.S. fraction of the same low rank coal were then maintained at a temperature of 150°C in air for a period of one week. The oxidized dust and a fresh sample were then exposed to air at room temperature for two days before test. The explosibility characteristics of the fresh and oxidized dusts were then determined, the values obtained for the explosions of 0·15 g in oxygen being given in *Table 5*. Oxidation at 150°C has resulted in an appreciable decrease in both the average and maximum rates of pressure rise while the maximum pressure developed is well below the value obtained with the fresh coal dust.

DISCUSSION

The experiments carried out on the effect on coal dust explosibility of (*a*) the addition of inert dust, (*b*) the prior oxidation of the coal fraction and (*c*) the blending of low and high rank coals yield results which do not

favour the 'volatile' theory of explosion propagation. If a coal dust explosion is propagated by the combustion of inflammable volatile decomposition products then an abrupt change in the explosibility characteristics can be expected when the volatile matter yielded by the coal is insufficient for propagated gaseous inflammation. That is to say, a sudden change in explosibility characteristics should be obtained when the rank of the coal is increased to a certain value. Coals of higher rank would then give

Table 5. Effect of atmospheric pre-oxidation at 150° C on the explosibility in oxygen of 0·15 g quantities of the −300 B.S.S. fraction of high volatile coal

State	*Maximum pressure lb./in.²*	*Rate of pressure rise lb./in.²*	
		Average	*Maximum*
Unoxidized	41·5	3580	9950
	42·5	3060	9950
	41·5	2240	7500
Oxidized	35·5	1280	4980
	35·5	1420	2860
	36·5	1380	2490

explosions in which the major factor governing the explosion rate would be the rate of oxidation of the solid particle by gaseous oxygen.

The variation of coal dust explosibility characteristics with rank in oxygen and oxygen–nitrogen mixtures containing 55 and 25 per cent oxygen (*Figures 7, 8, 9*) show in each case a smooth increase in explosibility with decrease in rank. Coals containing 6·4 and 7·1 per cent volatile matter (d.a.f.) are certainly incapable of yielding sufficient inflammable volatile matter to give propagated gaseous inflammation and it is difficult to visualize a sudden change in the explosion mechanism in view of the regular variation of explosibility with rank obtained. The increase in explosion rate with decrease in rank can be explained by the increase in heat radiation resulting from the burning of the volatile constituents around the residue produced by the thermal decomposition of the partly oxidized coal particle. The increase in temperature required to cause particle decomposition is achieved by the heat evolved during the initial oxidation of the coal particle. The formation of a flame 'pocket' around each particle will result in a greater rate of heat transfer to neighbouring particles with a consequent increase in explosion rate.

Air oxidation of the −300 B.S.S. fractions of a high volatile coal at 150° C effects an appreciable decrease in explosibility. Such oxidation will influence the reactivity of the coal particles far more than the nature and inflammability of the coal decomposition products. The observed effect of oxidation can then be easily explained if the reaction initiating explosion is a gas–solid oxidation reaction.

The addition of increasing amounts of inert dust to a fixed quantity of coal dust was found to give a progressive decrease in explosibility with a rapid decrease to zero as the extinction value is approached. A study of the relative inflammability of dusts by the author[1] has shown that the

quantity of inert dust required to suppress propagated combustion in oxygen increases rapidly with decrease in rank up to volatile contents of 20 to 25 per cent and increases at a lower, almost linear, rate with further decrease in rank. It is considered that the rapid increase in relative inflammability with decrease in rank observed with fairly high rank coals is due to the change in reactivity of the coal particle which governs the rate of oxidation and therefore the heat radiated. The glowing coal particles will then be the source of heat radiation, and comparatively small quantities of inert dust will be required to intercept and absorb the heat radiated. As the rank of the coal decreases the burning of volatile decomposition products will increase the heat radiated by increasing the volume and temperature of the radiating source. The quantity of inert dust will then have to be increased considerably to absorb most of the radiant heat emitted from a source which has increased both in volume and temperature.

The effect of blending high and low rank coals is also significant. The fact that the explosions produced have all the characteristics of the other high rank coals which could be exploded without blending suggests that the small quantity of low rank coal has merely increased the rate of heat transfer to the unburnt particles, so enabling a gas–solid oxidation rate to be achieved which will give propagation of combustion.

CONCLUSIONS

The measurement of the maximum pressures produced by the explosions of sized fractions of coal dusts in oxygen and the various oxygen–nitrogen mixtures has shown that the observed pressures are considerably lower than those calculated from analysis of the gaseous combustion products. Factors such as incomplete combustion, non-uniform distribution of the dust and the comparative transparency of gases to radiant heat can be suggested as possible explanations of the low values of maximum pressures obtained.

Figures 7, 8 and *9* show that the average rate of pressure rise shows the greatest variation with rank for coals of 6 to 20 per cent volatile matter using oxygen dispersion; for coals of 15 to 30 per cent volatile matter in a 55 per cent oxygen mixture, and from 22 to 36 per cent volatile matter when dispersed in a mixture containing 25 per cent oxygen. It may be reasoned that in oxygen the explosibility of the coals of 6 to 20 per cent volatile matter is determined by their reactivity to oxygen, the change in reactivity of the lower rank coals being obscured by the rapid burning of the volatile products in oxygen. Using a dispersion medium containing 55 per cent oxygen, coals of less than 15 per cent volatile matter are not sufficiently reactive to be ignited in this medium by an electric spark while the explosibility of coals of 15 to 30 per cent volatile matter vary according to their reactivity until the burning of volatile matter around each particle begins to overshadow any variation in reactivity. During explosions in a 25 per cent oxygen mixture the effect is even more marked with the explosibilities of practically the whole range of the coals which can be ignited being determined by their reactivity with the reduced rate of combustion of volatile matter assisting but never determining the rate of explosion.

Studies of the effect on coal dust explosibility of (*a*) pre-oxidation of the coal dust, (*b*) addition of inert dust and (*c*) the blending of low and high rank coals provide additional evidence of the importance of the surface reactivity of the coal particle in the initiation of explosion. It is therefore considered that in the explosion of coal dusts by electric sparks the initial heat-liberating reaction is that between gaseous oxygen and the particle surface. With the low rank coals not only is their surface reactivity higher than that of high rank coals but that any thermal decomposition subsequent to and as a result of the initial surface oxidation provides inflammable vapours which by their combustion around the particles result in an increased rate of heat transfer and therefore explosion rate. The greater the oxygen concentration the higher the rate of the surface oxidation and the more rapid the combustion of the volatile products.

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Self Combustion of Acetylene III—Effect of Oxygen and Ethylene Oxide

W. W. ROBERTSON and F. A. MATSEN

The self combustion of acetylene is promoted by the addition of small amounts of ethylene oxide and oxygen. Benzene formation appears to go through a different initiation mechanism from that of the bulk of the reaction; it appears to be wall inhibited.

WHEN pure acetylene is heated at 1 atm to 510°C thermal ignition occurs which produces large amounts of carbon, polymer, and hydrogen plus some benzene, ethylene and methane. Reaction occurs below this temperature[1] and produces essentially the same gaseous products. The addition of 1 per cent nitric oxide reduces both the benzene and ethylene concentration by at least 90 per cent and raises the ignition temperature by 100°C. These observations suggested that the non-free radical benzene formation was a key reaction in the production of free radicals for ignition process by way of the following mechanism:

$$A + A \longrightarrow A_2$$
$$A_2 + A \longrightarrow A_3$$
$$A_3 + A \longrightarrow B + A^*$$
$$A^* \longrightarrow C_2H + H$$

A^* was thought to be an excited acetylene molecule which carries most of the 134 kcal liberated in the formation of benzene. The free radicals produced would initiate many reactions, including the formation of benzene.

EXPERIMENTAL PROCEDURE

All experiments were performed on a flow system. The reactor was a heated *Vycor* tube 60 cm long by 38 mm in diameter, and temperatures were measured by a thermocouple in contact with the exterior wall. Commercial grade acetylene was passed through a purification train and flow gauge into the reactor at rates of 0·005, 0·01 or 0·02 ft.^{3}/min. The components of the purification train were as follows: (*1*) 40 per cent $NaHSO_3$ in water, (*2*) concentrated chromic acid, (*3*) 50 per cent $HgCl_2$ in hydrochloric acid, (*4*) 36 per cent KOH in water, (*5*) concentrated alkaline $Na_2S_2O_4$, (*6*) 36 per cent KOH in water and (*7*) anhydrous $CaSO_4$. It was assumed that the concentrated alkaline sodium hydrosulphite reduced the oxygen concentration to a negligible value. Small amounts of oxygen and of ethylene oxide were metered into the acetylene stream prior to its entering the reactor.

The reaction products were passed through a Perkin Elmer 12C infra-red spectrometer for analysis. Calibration curves for CO, CO_2, C_2H_4, *etc* were obtained in acetylene at a total pressure of 1 atm to approximate conditions existing in the reaction products. Ketene and carbon monoxide absorb at approximately the same frequency and the analysis involved obtaining the combined band first and then absorbing out the ketene to get the CO band alone.

RESULTS AND DISCUSSION

The addition of small amounts of oxygen lowers the ignition temperature of the acetylene and increases the amount of benzene and ethylene which is produced (see *Figure 1*). Carbon monoxide and small quantities of glyoxal and ketene* are also formed but the quantity of oxygen present is too low

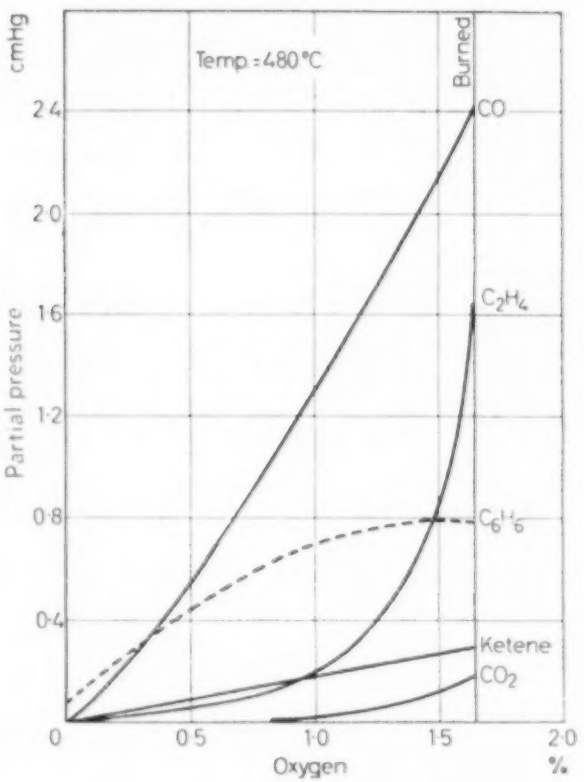

Figure 1. The effects of small amounts of oxygen on the self combustion of acetylene at pre-ignition temperatures. (The oxygen concentration required for ignition at a given temperature is a sensitive function of the condition of the surface of the reactor; however, the shapes of the curves remain essentially unchanged)

to support the oxy-acetylene flame. The combustion of acetylene in the presence of small amounts of oxygen is very similar to the self combustion in pure acetylene, but it is clear, however, that oxygen is initiating chains which are propagated in the acetylene. On increasing the oxygen concentration, the benzene pressure rises rapidly and flattens out while the ethylene pressure rises exponentially. This suggests a different initiating mechanism for the two compounds. Furthermore, oxygen, directly or indirectly, must be diverting some of the free radicals which, in the absence of oxygen, would produce benzene by a free radical process. A clue to this diversion

*Ketene has not until now been reported in an oxygen-acetylene system.

is found in the variation of the flow rate—as the flow rate is increased, in the presence of oxygen, the benzene concentration increases (see *Figure 2*).

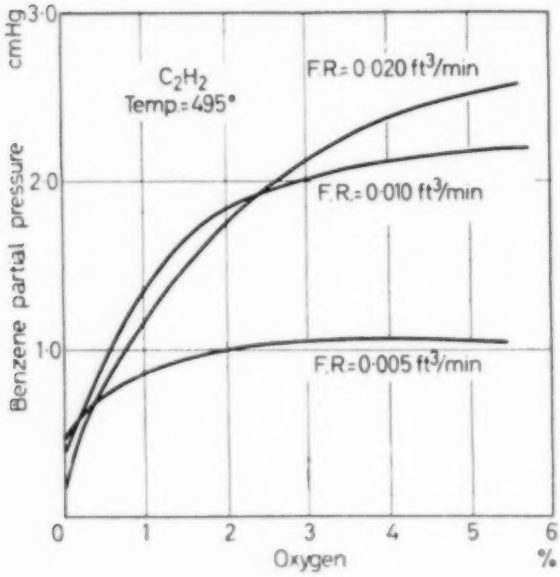

Figure 2. The partial pressure of benzene as a function of oxygen concentration at various flow rates

These results suggest that the inhibition step occurs on the wall. It is known that peroxides deposit on the walls and these may be benzene inhibitors. Cleaning the tube with acetone enhances the rate of benzene formation, and the washing gives a test for peroxide.

The effect of oxygen on benzene formation at various temperatures is given in *Figure 3*. The apparent activation energy for benzene formation is 70 kcal, independent of oxygen concentration.

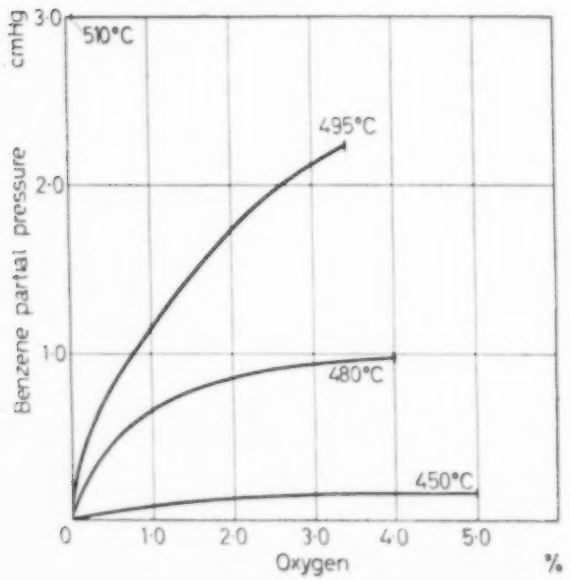

Figure 3. The partial pressure of benzene as a function of oxygen concentration at various temperatures

In *Figure 4* the spontaneous ignition limits are shown as a function of temperature and oxygen partial pressure. The areas covered by previous investigators[2-6] (*I*) and in the present work (*II*) are outlined.

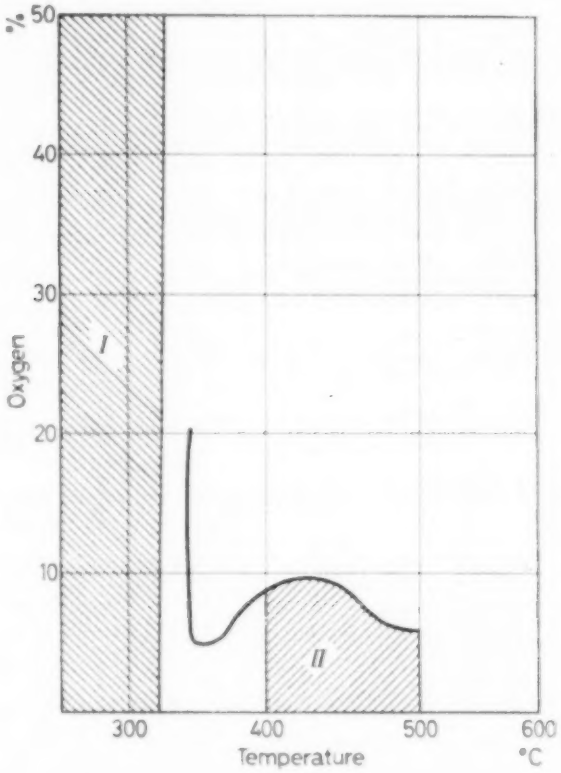

Figure 4. Oxygen concentration required for spontaneous ignition at various temperatures. The present work is confined to region II, most previous work to region I

Most of the earlier investigations of the reactions in the oxygen–acetylene system have been carried out below 350 °C and at pressures below 1 atm. It was found that the rate of reaction increased, levelled off and then decreased with increasing oxygen concentration[2-5]. The rate of propagation of a flame ignited by a hot wire in gas at 300 °C behaved similarly[6]. The results at higher temperatures differ from the earlier ones in that the rate, as measured by ethylene concentration, continues to increase until ignition occurs. This is attributable to the fact that the temperature of the reaction is closer to the self ignition temperature of acetylene, so that the free radicals produced by oxygen can initiate self combustion chains in the acetylene. These chains cannot be sustained at the lower temperatures and lower pressures. It was also found that the rate decreased with additional surface[4], which is in qualitative agreement with our observations on flow rate. The activation energy observed for the total reaction[3, 4] is only half of that observed for the benzene formation. No formaldehyde was found, which accords with previous observations that formaldehyde is very rapidly oxidized in the presence of acetylene[3].

Ethylene oxide produces free radicals at these temperatures and so should be an effective ignition initiator. In addition there should be no inhibition

by destruction of free radicals by reaction with peroxides at the wall. That this is so can be seen from *Figure 5*. At 495°C only 0·6 per cent ethylene oxide, as contrasted to 2·8 per cent oxygen, is required for ignition. Furthermore, the benzene concentration increases exponentially, indicating that there is no inhibition such as was found with oxygen initiation. A

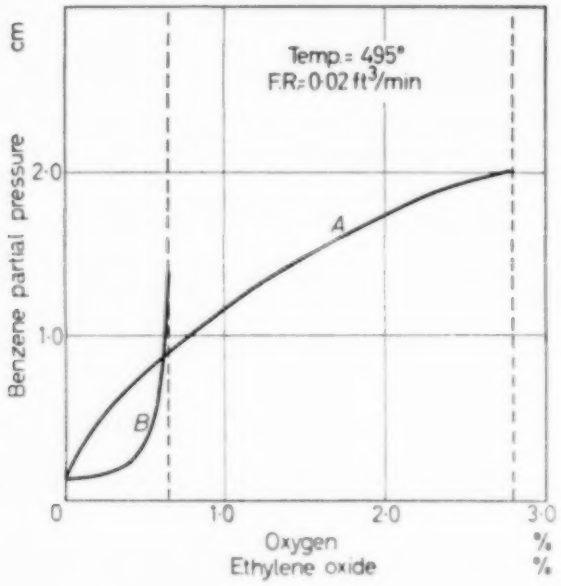

Figure 5. The different effect of ethylene oxide and oxygen on benzene formation: A *oxygen added;* B *ethylene oxide added*

comparison of results obtained with pure acetylene plus oxygen show that, in area *II*, the hydroxylation mechanism postulated by earlier workers can at most be important in the initiation step.

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A Cool Flame Phenomenon in the Combustion of Acetylene

W. W. ROBERTSON and F. A. MATSEN

Ignition limits were determined on adding small concentrations of oxygen to heated acetylene in a flow system. A 'cool flame' was observed when the reactor contained fresh carbon.

WHEN pure acetylene is heated at 1 atm pressure to a temperature of about 500° C, thermal ignition occurs with the production of large quantities of carbon, polymer and hydrogen and small quantities of benzene, ethylene, ethane, methane, *etc.* Reactions occurring below the ignition temperature produce essentially the same gaseous products[1].

When small quantities of oxygen are added to the heated acetylene at pre-ignition temperatures, the reaction products of self combustion occur in larger concentrations, together with small quantities of carbon monoxide, glyoxal, ketene, and carbon dioxide[2]. The temperature of intiation of the thermal ignition of the acetylene is also lowered; this research investigated some of the factors influencing the ignition temperature.

EXPERIMENTAL PROCEDURE

The reactor consisted of a heated *Vycor* tube through which a measured flow of pure acetylene and of oxygen was maintained[1, 2]. The gaseous products were passed through a Perkin-Elmer Model 12C infra-red spectrometer for analysis. The temperature of the reactor was set at a chosen value and the oxygen concentration increased gradually until ignition occurred. It was found necessary to standardize the reactor surface, since a clean surface, a fresh carbon surface and an aged carbon surface gave different results. The reaction products were cleaned from the reactor by burning in an oxygen atmosphere. Old carbon was left in the tube by incomplete combustion in the cleaning process. Fresh carbon was produced by heating the reactor and adding a burst of oxygen to promote ignition, at which stage the oxygen was turned off and the reactor cooled before starting the run.

RESULTS AND DISCUSSION

Two sets of ignition curves, one for a clean reactor and one for a reactor containing fresh carbon, for two different flow rates, 0·02 and 0·01 ft.^{3}/min, are presented in *Figure 1*.

The solid curve in *Figure 1B* shows the oxygen concentration required for ignition plotted as a function of temperature for the reactor containing fresh carbon and for a flow rate of 0·02 ft.^{3}/min. The solid point on the

left-hand vertical limb of the curve represents the oxygen concentration attained at that temperature without ignition (see also curve *1C*). The ignition curve was arbitrarily drawn just to the right of the solid point. In a narrow zone about the broken line there occurred pressure bursts which were periodic and vigorous at the lower temperatures (300° to 350°C) but which changed to single or double weak pulses at the higher temperatures (450° to 500°C). The periodic pressure bursts did not continue as the oxygen concentration was raised above that represented by the broken line. This phenomenon seemed to be the one generally described as a 'cool flame'. The 'cool flame' merged into the ordinary flame at around 300° and 500°C. A temperature rise in the reactor accompanied the 'cool flame' and there was an increase in the glyoxal concentration in the reaction products. At the lower flow rate, 0·01 ft.^{3}/min, the 'cool flame' appears to set off the normal flame, see *Figure 1D*.

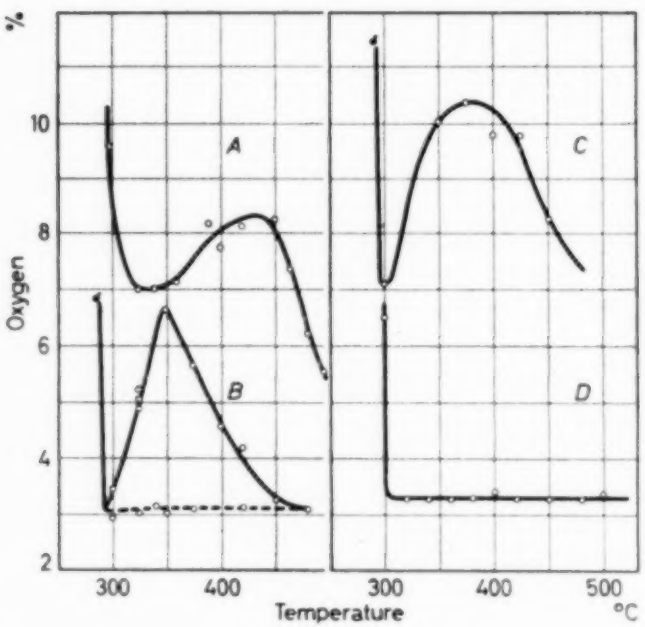

Figure 1. Ignition curves: A *clean reactor, flow rate 0·02 ft.^{3}/min;* B *reactor containing fresh carbon, flow rate 0·02 ft.^{3}/min;* C *clean reactor, flow rate 0·01 ft.^{3}/min;* D *reactor containing fresh carbon, flow rate 0·01 ft.^{3}/min*

Figures 1A and *1C* give the ignition curves at the flow rates of 0·02 and 0·01 ft.^{3}/min, respectively, for the clean reactor. The shapes of the curves are the same as in *Figure 1B*, but there is no 'cool flame'. Also, the oxygen concentration required for ignition is about twice that required when the reactor contains fresh carbon. The reactor with old carbon yielded erratic results falling between curves *1A* and *1B* or *1C* and *1D*.

The curves show a remarkable similarity to the plot of ignition pressure against ignition temperature for ethane–air mixtures obtained by D. T. A. Townend and E. A. C. Chamberlain[3,4]. They obtained the dip in the ignition curve on the addition of aldehyde. In the acetylene system it would appear that a similar reactive intermediate is formed at low tempera-

tures and low oxygen concentrations, and that the intermediate is either decomposed on a clean surface or its formation is catalyzed on a freshly formed carbon surface.

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Flame Zone Studies III—Techniques for the Determination of Composition Profiles of Flame Fronts

R. M. Fristrom, R. Prescott and C. Grunfelder

The understanding of combustion processes can be greatly increased by a determination of the composition of a flame front as a function of position. This paper describes techniques for making such measurements. Aerodynamic and temperature profiles are available from other studies. The information can be used to determine reaction rates and to deduce reaction mechanisms and activation energies. The information available through this study and other experimental studies of flame fronts is equivalent to that obtained in the most extensive conventional reaction kinetic studies, and offers a fertile field for the study of many very fast reactions. Since these techniques are new, detailed consideration is given to the question of reliability and interpretation of the results. Critical experiments are cited to show the existence of a single set of composition profiles that uniquely describe a laminar flame front and to establish that they can be reproducibly and accurately determined by these techniques. It is concluded that composition profiles can be measured with useful precision.

The clarification of many combustion problems, particularly those of chemical interest, requires a more detailed analysis of the reaction zone than has previously been available. Of particular interest in the study of high-temperature reaction kinetics in premixed laminar flame fronts are 'composition profiles'. These profiles are graphs relating composition with either position, elapsed time, or temperature. The primary data consist of analyses of gas samples taken at various positions within the flame front and recorded as concentration against normal distance through the flame front. The techniques of making the associated aerodynamic and temperature measurements have been discussed previously[1,2]. These data, together with calculations or measurements of the thermal conductivity and diffusion constants of the mixtures, can be used to study the kinetics of flame reactions. Such studies should provide the answer to a number of fundamental questions about flame processes.

The techniques and problems encountered in the determination of composition profiles are discussed in this paper while data from a typical hydrocarbon flame have been analysed and interpreted in a subsequent article[3]. The experimental problems will be discussed in some detail since these techniques are new to flame studies; estimates have been made of their reliability. The data appear to give a reasonable approximation to the course of combustion in the flame fronts, and the results represent information that is available from no other source.

EXPERIMENTAL METHODS

The experimental methods are simple in concept but complex in execution. They consist of withdrawing and quenching* small samples of the flame

*Quenching refers to the process of rapidly stopping a reaction in the sample by lowering the pressure and temperature.

gases at various known positions and then analysing these samples. This is the classic method of reaction kinetics, but a number of difficulties are involved: (*a*) a suitable probe must be found; (*b*) the sampling rate must be sufficiently small that the withdrawal will not disturb the flame front or impair the spatial resolution of the sample, yet be large enough for analysis; and (*c*) the sample must be withdrawn rapidly enough to quench the reaction.

A technique for making these measurements has been evolved, employing sampling with a quartz microprobe and analysing the resulting sample with a mass spectrometer. The probe position, relative to the luminous zone of the flame, is determined photographically. A study has been made on a stoichiometric, propane–air flame at a pressure of $\frac{1}{4}$ atm.

Burner

A conical flame was maintained on a 1 in. burner with a constant-velocity nozzle. The burner system and auxiliary photographic equipment are described elsewhere[1-4]. The positional stability of this flame allows high resolution even with sample times of the order of 5 min. The stability of the flame was tested by focusing the cross hairs of a telemicroscope on the violet-blue interface in the luminous zone of the flame and observing the flame over a 5 min period. The maximum excursions observed during this period were 0·03 mm. Photographs taken with half-hour exposure times show no evidence of long-term drift.

Materials

The propane was of high purity (99·7 per cent) and was checked on the mass spectrometer by comparison with other high purity samples. The air used was taken directly from the laboratory where humidity and temperature were known and controlled. The initial temperature of the gas was determined with a thermocouple.

Microprobe

The critical tool of this experiment is the probe for withdrawing samples, which must withstand temperatures as high as 2000°K; it must be small and of such material that it does not disturb the flame, and it must be designed so that the sample is rapidly quenched. Previous work[1-3] showed that a quartz probe was satisfactory for flames up to 2000°C*, and that there was little dependence of the results on the diameter of the orifice between 5 and 100 μ. R. FRIEDMAN[5] compared quartz probes of this type with water-cooled probes and concluded that both probe types were satisfactory. The pressure inside the probe can be varied from a few mm down to 100 μ of mercury without affecting the results. The technique is not completely insensitive to probe design, as pyrolysis occurs in very slender probes, but this can be easily overcome by proper design. It was usually found that if the probe was clean†, small enough and properly oriented, it

*This is possible because the probe is cooled by radiation below its 1700°C softening point.

†Probes were cleaned by immersion in hot concentrated nitric acid.

entered the flame with no visible effect. Generally, it was possible to avoid distortion of the flame front if the probe was introduced from the hot side of the flame along the streamlines of flow. Turning the probe at an angle or introducing the probe from the cold-gas side of the flame resulted in distortion of the flame front because of the wake of the heavy connecting tubing. Even so, however, consistent results were obtained if the local luminous zone was used as the reference surface. A diagram of probe flow is given in *Figure 1*.

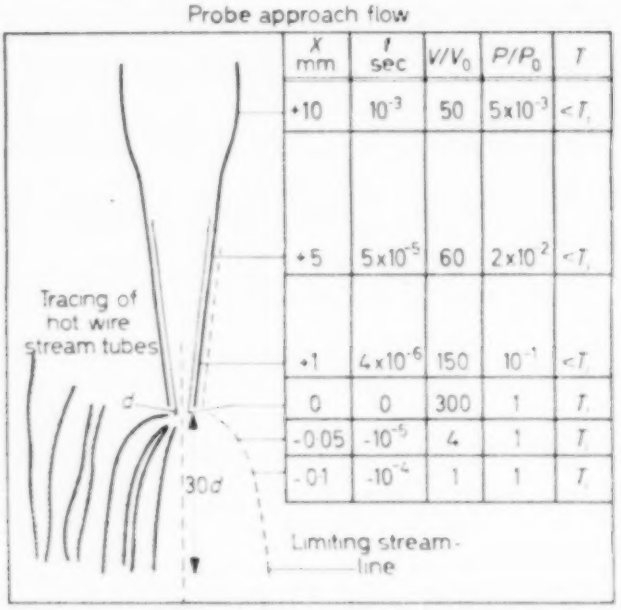

Figure 1. Microprobe flow patterns

Probe position determination—The position of the probe relative to the luminous zone of the flame was determined photographically, a camera with a sharp plane of focus being used[1]. This arrangement allowed centring of the probe to $\pm 0{\cdot}5$ mm. The position of the probe could be adjusted with a micromanipulator and monitored visually on the focusing screen of the camera. Photographic measurements allowed a determination of the normal distance from the probe tip to the centre of the luminous region with a reproducibility of 0·02 mm. Photographs were usually taken at the beginning and end of the sampling period. The probe position was monitored visually during the period of sampling.

Analytical procedure

Sampling—The sample was taken from the probe into a 3 l. bulb which was filled up to a pressure of 100 μ (*Figure 2*). The sampling period lasted from 3 to 5 min.

Analysis—The 300 μl. sample was then analysed on a mass spectrometer. The instrument used for this work was the Consolidated Engineering Co. Model 21-610. Satisfactory analytical results can be obtained with careful work using an internal standard rather than the more common method of

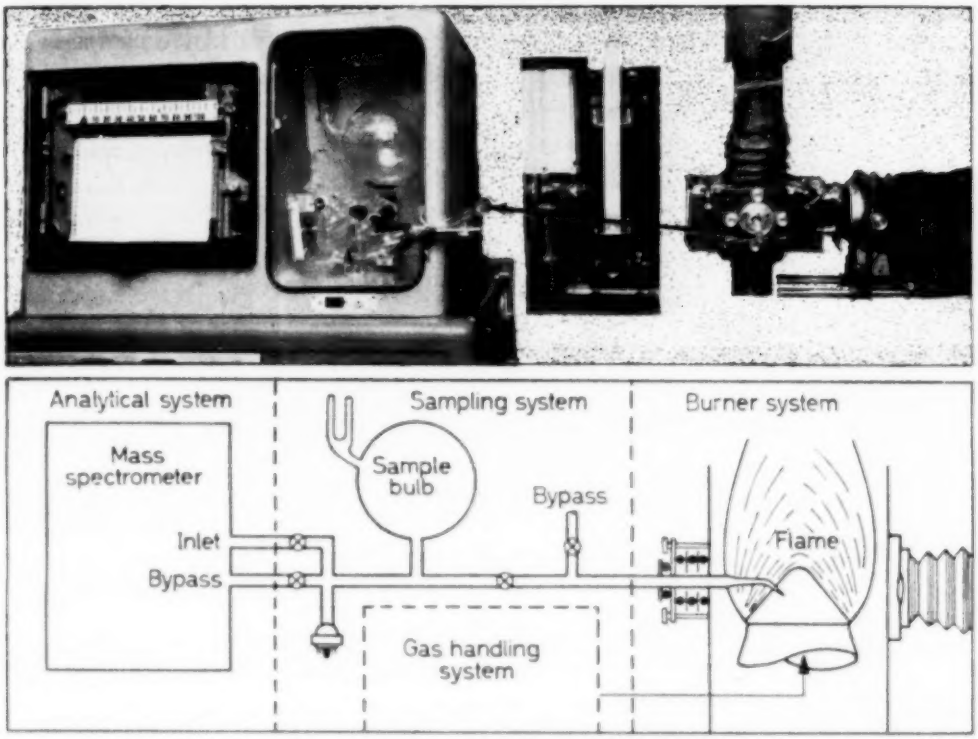

Figure 2. Flame sampling apparatus

absolute sensitivities. The argon present in the air provided a convenient standard whose atomic mass fraction was not affected by the combustion process. The primary data were numbers of molecules of each species relative to argon; these were then reduced to mole fractions. The average reproducibility of the instrument using an internal standard is 1 per cent as compared with 3 per cent using absolute sensitivities. This gain is primarily due to the insensitiveness of the internal standard method to the long term stability of the instrument.

Because of the complexity of the analysis (analytical results are presented for some thirteen components and seven other species are shown to be absent) it was necessary to separate the sample into two parts. A convenient separation was provided by a liquid nitrogen trap which quantitatively separates the permanent gases from the less volatile components.

Using this technique, it was possible to find unique mass peaks for the majority of the species, but in the remainder it was necessary to correct the peak heights for interference by one or more molecular species. Each analysis presented a separate problem, which is discussed elsewhere[7].

Table 1 outlines the procedures which have been developed here: these are adequate for mixtures of simple hydrocarbons (up to propane) in the presence of carbon monoxide, carbon dioxide, hydrogen, oxygen, nitrogen, argon, helium and water, while several other components, such as nitric oxide, formaldehyde, ethyl alcohol and methyl alcohol, could have been

handled had they been present. It was possible to demonstrate the absence of many other components in this system, such as higher hydrocarbons and oxygenated compounds—alcohols, aldehydes, ketones, acids, peroxides and oxides of nitrogen.

Table 1. Analysis of propane flame gases by mass spectrometry

Species	*M/e*	*Interfering species*	*Trap*	*Maximum concentration per cent*
A	40	*None*	*Yes*	1
CO	12	CH_4	*Yes*	8
CO_2	44	C_3H_8	*No*	12
H_2	2	CH_4	*Yes*	4
H_2O	18	*None*	*No*	16
N_2	28	CO	*Yes*	75
NO	30	*None*	*Yes*	<0·05
CH_4	15	*None*	*Yes*	0·3
C_2H_2	26	C_3H_8, C_3H_6, C_3H_4, C_2H_6, C_2H_4	*No*	0·4
C_2H_4	27	C_3H_8, C_3H_6, C_3H_4, C_2H_6	*No*	0·4
C_2H_6	30	OCH_2	*No*	0·5
C_3H_4	29	C_3H_8, C_3H_6	*No*	<0·1
C_3H_6	41	C_3H_8	*No*	0·4
C_3H_8	43	*None*	*No*	4
OCH_2	30	C_2H_6	*No*	<0·1
CH_3OH	31	*None*	*No*	<0·1
C_2H_5OH	45	$C^{13}O_2$	*No*	<0·1
Higher hydrocarbons	>48	*None*	*No*	<0·2
Oxygenated compounds	>48	*None*	*No*	<0·2
O_3	*Destroyed by sampling process*			
H_2O_2	*Destroyed by sampling process*			
Free radicals	*Destroyed by sampling process*			
Nitrogen oxides	*No analysis*			

Some molecules are too unstable for these sampling techniques, so that no estimate could be made of the concentration; principally these are hydrogen peroxide*, ozone*, free radicals and atoms.

Several species presented special analytical problems. The data for hydrogen, in and beyond the luminous region, furnished the only really unsatisfactory result in these studies. Their spread limits the usefulness of the results, though this may be a sampling problem. The results in the colder regions are quite satisfactory and reproducible.

Water deserves special mention because of the difficulties of adsorption, but experience has shown that, with moderate care, significant results can be obtained[5]. The spread of results was larger than was desired, but the

*Both hydrogen peroxide and ozone were quantitatively absent (< 0·01 per cent) in a methane diffusion flame (private communication, S. FOSTER, also ref. [5]) where their concentration might be expected to be higher than in a laminar flame, such as is considered here.

importance of water as a component of flame gases warranted the acceptance of the best available data. It is believed that much of the difficulty that has been experienced in the past was due to the use of samples with excessively high partial pressures of water, combined with the effects of allowing the samples to stand for long periods of time. In this work the partial pressure of water did not exceed 10 μ and the analyses were completed within 15 min of sampling.

Carbon monoxide analysis is difficult because it is necessary to use a peak of very low sensitivity which is interfered with by methane.

Calibration—Since the mass spectrometer is not a primary analytical instrument, it is necessary to provide known standard mixtures. Two techniques were used. In the first method the gases were metered into the burner and sampled*, while in the second a batch sample was introduced from a bulb. Known synthetic mixtures were made up by gas handling techniques. No systematic differences were observed between calibrations obtained using the two methods.

INTERPRETATION OF COMPOSITION PROFILES

Two questions arise in connection with composition profile studies—first, can a flame be described by a single set of composition profiles? and, second, can such a profile be measured by the techniques being discussed?

The existence of unique composition profiles

It is generally assumed in the interpretation of flame phenomena that a one-dimensional model provides a reasonable approximation for a flame[2, 9, 10]; this follows as an immediate consequence of the assumption that the reaction course is everywhere the same in the flame front. Such a model is an approximation, whose validity is subject to experimental verification. The assumption that the flame is unbounded or of very great extent may be questionable since, in the usual Bunsen burners, the ratio of flame thickness to burner diameter varies between 0·05 and 1. Spark-ignited flames, which provide examples of unbounded flames of finite extent, are not time-independent since the flow relationships between the normal and tangential components vary with radius. In this instance, however, there may be a range of diameters within which the one-dimensional model provides a good approximation.

A study has been made of the validity of one-dimensional models using the particle track technique. It was found that, in so far as time, normal gas velocity, gas density and temperature are concerned, a one-dimensional model is adequate. The composition profiles show this same regularity (*Figure 3*). Previous results[2], together with the present study, provide an experimental justification for the application of one-dimensional models to flame problems.

The unidimensional character of flame front composition profiles was established by showing that the composition of the flame gases was

*With water, the sample was taken from the completely burnt gas where the water concentration could be calculated. It has been pointed out that this might be somewhat in error owing to diffusion into and out of the flame[3].

dependent only upon the coordinate normal to the flame front and was independent both of position along the flame front and of external variables such as gas velocity, flame geometry and burner diameter. Experimentally, this coordinate was the distance normal to the reaction surface as visualized by the luminous zone of the flame. The origin was taken as the surface formed by the centre of this region, and the direction of gas flow taken as positive. This origin was approximately marked by the interface between the blue luminosity of C_2 and the purple luminosity of CH.

The first invariance to be considered was that with respect to position along the flame front. The fact that it was possible to construct satisfactory composition profiles without any special precautions in reproducing position along the flame front provided evidence of unidimensionality. It was desirable, however, to determine over what region this invariance extended

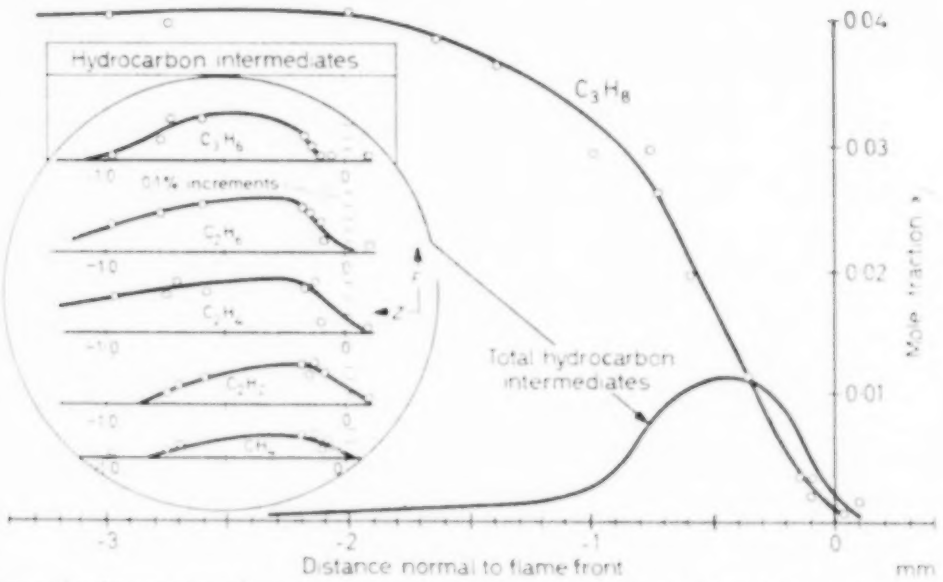

Figure 3a. Experimental composition profiles—mole fraction against distance (propane and intermediate hydrocarbons)

and, for this purpose, several samples were taken at identical normal positions, but at widely varying positions along the flame front. The results for three representative positions are shown in *Figure 3b**.

Composition profiles appear to be insensitive to burner gas velocity, burner diameter and flame shape. Evidence for this is given in *Figure 3* which compares the present data with that obtained previously[1]. The agreement is good. The results cover three different gas velocities, two different burner diameters and two different flame geometries. Analyses taken at these three positions can be adequately described by a single set of composition profiles.

The composition profiles are functions only of the initial state of the gas —composition, temperature and pressure—and are independent of external

*The region beyond the luminous zone is not included in these comparisons because the carbon monoxide oxidation that occurs in this region is not strongly coupled with the flame propagation.

variables such as gas velocity, burner diameter and flame geometry. This, taken together with the work on temperature profiles[2], provides strong evidence of the applicability of a unidimensional theory to actual premixed laminar flames. Only the concentration profiles of the unstable species have

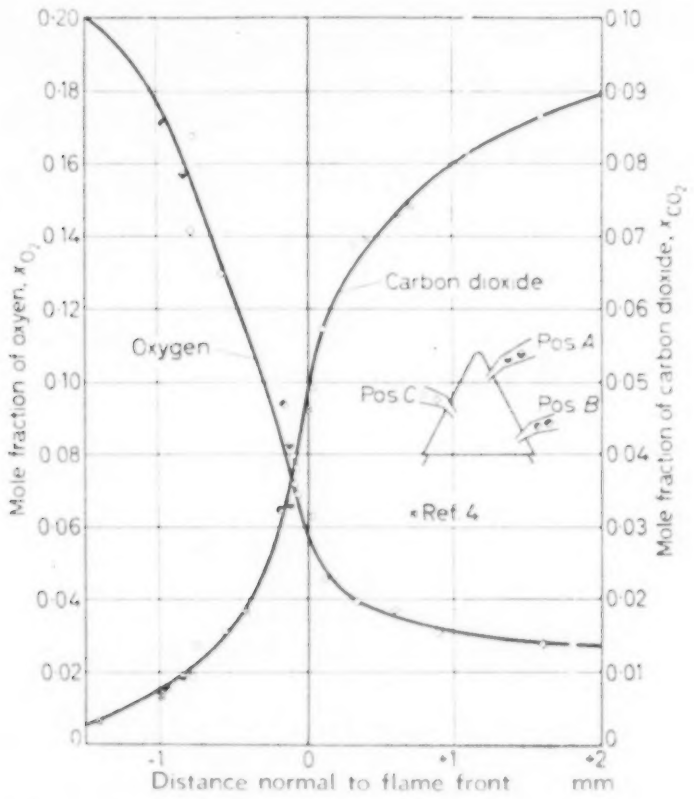

Figure 3b. Experimental composition profiles—mole fraction against distance (oxygen and carbon dioxide)

not been investigated, and it would be surprising if they did not follow the same general pattern. In this study, the unidimensional model has been verified experimentally, and such a model probably has a general applicability. However, it should be pointed out that the model is definitely not applicable to certain flame systems, such as flames which are cellular or turbulent, and, that in a more complex system where many reactions occur simultaneously, they may not all be strongly coupled with the flame propagation*. The more general conservation equation, $\rho v a = \text{constant}$, where ρ is the density of the gas, v is the normal velocity and a is the cross-sectional area measured at right angles to the velocity measurement, must be used. The stream tube expansion ratio a/a_u, where a_u is the cross-sectional area in the cold gas, is also a unidimensional function of distance.

*An example of such a reaction is the oxidation of the carbon monoxide formed as an intermediate in the propane–air flame. Beyond the luminous region of the flame, this reaction appears to be dependent on time rather than on distance and to have little or no effect on the propagation rate of the flame. This type of pseudo-homogeneous reaction, which is initiated and carried along by a flame system, is not discussed here. Mixed hydrocarbon–boronhydride double flames provide another example of this phenomenon[11].

An analogous case is the treatment of one-dimensional hydrodynamic flow in a duct of varying cross-section. Within these limitations, the model provides an excellent framework for studies of flame fronts.

Justification of microprobe sampling techniques in flame front studies

The justification of a new experimental technique is difficult when it is not possible to make a direct comparison with results from an accepted method or theory. In general, the justification in the present work consists in showing that the results are reproducible and reasonable, and that they can be correlated with independent data.

Effects of probes on flame fronts

The problem of the effect of probes on flame fronts is a complex one. It is believed that there is sufficient evidence to indicate that the disturbance introduced by a suitably designed probe is not serious. The effect of a probe on a flame can be threefold, namely, aerodynamic, thermal and catalytic.

Aerodynamic effects on probes—Problems of probe aerodynamics can be classified as either external or internal. The external flow determines the effect of the probe on the flame; the internal flow, which will be discussed later, determines the efficiency of the sample quenching. They are interrelated since the two geometrical requirements are opposed. Compromise designs have been made which are suitable for the present work, and probes were designed to minimize disturbance of the flame front when introduced along the direction of the streamlines. Other orientations distorted the flame, and the interpretation of the sample became more difficult. The results, using the local luminous zone centre as a reference surface, were not strongly affected either by probe orientation or by local distortions of the flame front. This indicated that aerodynamic disturbances did not affect the microscopic flame profiles.

The problem of the distortion of flow by sample withdrawal has been considered by P. ROSEN[12], who chose for his model a uniformly distributed disk sink; flow was assumed to be incompressible and irrotational. These results allowed an estimate to be made of the distance ahead of the probe at which a particular level of velocity distortion occurs and of the flow time taken by a stream tube from this point to the sample point. Using typical parameters from the probe sampling in the present work—probe diameter, 1×10^{-3} cm; sink strength, 300 and a normal flow velocity, 100 cm/sec—one predicts that the position of 10 per cent flow disturbance is 20 probe diameters ahead of the probe. This means that the flow is disturbed less than 10 per cent at distances greater than 0·1 mm ahead of the probe. This estimate has been verified by Schlieren pictures of the flow streamlines, which were visualized using the thermal wake of a Wollaston wire as a tracer. In order to obtain measurable pictures it was necessary to scale up the probe size by a factor of 10 (*Figure 1*). A gas element at the 10 per cent flow disturbance point reached the probe in less than 50 μsec, this time

representing one-tenth of the half life of the propane disappearance. The error in assignment of time to a sample can only be a fraction of this lag, and should be below 50 μsec in the worst case and probably negligible over most of the flame. The positional error is some fraction of the calculated disturbance distance region, *i.e.* less than 0·1 mm, a distance of the same order as the experimental resolution. No attempt is made to correct for the true position of the sample, for which the position of the tip of the probe is used, on the understanding that it is subject to an uncertainty smaller than $\pm 0{\cdot}1$ mm.

Thermal and diffusional effects of probes—Apart from the flow disturbance, which appears to be small, there are two other effects which a probe may have on a flame. One is that it may change the heat transfer into the sample region, and the other is that it may change the diffusional transfer of reactive species, such as radicals, into the sample region. Because of the low conductivity of quartz, the temperature of the probe will approximate to that of the gas throughout the flame front, lagging a few hundred degrees, perhaps, in the hottest part of the flame where radiation cooling is the greatest. Measurements of the surface temperature of the probe by optical pyrometer have verified this assumption in the burnt gas region. The question of diffusional transfer is discussed under sample interpretation.

Catalytic effects of probes—One of the principal objections to probe techniques in flame studies is the possibility of catalytic effects on the surface of the probe. These effects can be of two opposing types—a quenching or negative catalytic effect or a positive catalytic effect. The first would be important if the probe were much cooler than the surrounding gas, *e.g.* if it were metal or were water-cooled. This is not so with the hot quartz probe, for which acceleration of the reaction on the surface of the probe is a more serious problem. The quartz surface, if properly cleaned, shows no bright spots of catalytic activity. Catalysis on ceramic surfaces of coated thermocouples is discussed elsewhere[13, 14] and it is concluded that such effects can be made negligible.

Since the sample is taken ahead of the probe (*Figure 1*), any effect that the probe has on a sample entering the orifice is due to the disturbance of the feedback from the hot region environment of the flame. The mechanism of this feedback is twofold: thermal conduction and molecular diffusion—the small solid angle occupied by the probe should minimize these effects. A point of considerable importance is that deviations from the local conditions, *e.g.* radical concentration or stable species concentration, will tend to be erased by lateral diffusion and heat transfer. These problems are discussed in detail elsewhere[15].

These considerations indicate that the disturbances introduced by the probe are small and should show up as a shift in effective position of the sampling point.

The separation between the end of the probe which is measured and the actual average position represented by the sample is less than 0·05 mm. This small and approximately constant shift of the coordinate system does not appear to distort the relation between temperature and composition

profiles. Samples taken by inserting the probe from the cold gas and from the hot gas side of the flame give essentially the same results.

Quenching efficiency of the probes

The technique of studying chemical reactions by rapidly taking a sample and freezing the composition is the classical method of chemical kinetics. The difference between present techniques and the older ones lies in the use of a flow system and in the extreme rapidity of the reaction being studied. In flow systems, distance rather than time is the primary variable. Because of the short half life of the reaction—about 500 μsec—an exceedingly rapid method of quenching is required. The method used is rapid adiabatic expansion followed by cooling. Estimates of the quenching time are given in *Figure 1*. Quenching lags are of the order of 5 μsec; this delay is much smaller than the time resolution of the technique. The effect is in the opposite direction to the uncertainty of sampling position.

Internal aerodynamics and quenching

The problem of quenching depends on the history of the sample after entering the probe. Since it is assumed that the critical initial quenching is accomplished by pressure drop, the time–pressure history of the sample after entering the probe is important. This is a complicated problem, but in the present work measurements of the internal geometry of a typical probe enable one to make reasonable approximations. It is assumed that the orifice is sonic and that the sample is in thermal equilibrium with the walls. The probe is designed so that the pumping speed of each section is large compared with the section ahead of it. Thus, most of the pressure drop (a factor of 2500) occurs in the tapered section of the probe. Backing pressure varies from a few microns at the beginning of the sampling period to 100 μ at the end. 100 μ is chosen as representing the worst case, and a velocity distribution similar to measurements made on a 10° cone is assumed. The pressure drops to 0·1 of its original value in 5 μsec and to 0·001 of its original value in 50 μsec. The sample enters the cold part of the probe in a fraction of a millisecond. Such a sampling process should have a negligible effect on a reaction whose half life is 500 μsec.

Effects of wall reactions and free radicals

Because of the speed of flow through the probe, reaction will be confined to the slow-moving boundary layer which constitutes only a small fraction of the total sample (<3 per cent). If it is argued that the boundary layer is stripped off, then the residence time would not allow appreciable reaction to occur. It has been verified experimentally that there is negligible reaction of propane–air mixtures in a probe of this type, heated externally to the flame temperature. The effect of sample free radicals is limited by the rapid decompression time which is so short that no chain processes can be established. The free radicals are destroyed by diffusion to the cold walls of the sample bulb. The odd electron species, annihilated at the walls, show up as stable species (H as H_2, OH as H_2O, *etc*); their contribution can be ignored if the radical concentrations nowhere exceed the equilibrium

values in the burnt gas (in this case 0·03 per cent H and 0·1 per cent OH). The radical concentrations in the reaction zone may be higher, but are probably still negligible compared with any stable species[16]. This is a reasonable assumption and the fact that the results are independent of probe size and shape and of the cooling of the probe and the pressure inside it appears to justify it.

Sample interpretation

There has been some discussion as to whether the sample taken by a sonic probe in a concentration gradient field represents the composition at the sampling point or the flux past that point. In a flame, these two quantities are significantly different[3]. To resolve this question, a series of experimental and theoretical studies were undertaken[15], and the general conclusion was that, so long as diffusion and unperturbed gas velocities were small compared with the gas velocity at the probe throat* (sonic speed), the sample represented the concentration at the sampling point.

CONCLUSIONS

Using the techniques described in this paper, it is possible to determine experimental composition profiles that are useful in the detailed study of the course of reactions in flame fronts.

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*This ratio was always less than 1 per cent in the authors' experiments.

Recent Developments and Notes

THE RANDOM WALK MODEL OF FLAME PROPAGATION

H. EYRING, J. C. GIDDINGS and L. G. TENSMEYER, of the University of Utah, have recently propounded a new approach to the theory of burning velocity [*J. chem. Phys.* 24 (1956) 857]. They assume that a flame front moves forward at a rate determined by the random walk of chemical (potential) energy. The basis of their approach is to consider only one of the many processes that occur in a flame front. On analogy with the standard concepts in the theory of reaction rates, the calculation of flame velocity might be made at any point in a flame, since all points in the flame are moving at the same observed velocity. In separate regions of a flame, however, different processes preserve the stationary state. In some regions it is thermal conduction alone, while in others it is a complex interaction between reaction rate, diffusion and conduction which maintains the constant temperature profile. In the burnt portion, cooling and molecule recombination may be thought of as propagating into the burning gases at a velocity which is the observed flame velocity.

The calculations made by the authors are for the point of maximum reaction rate, on the assumption that, at some point in the flame, chemical reaction rate plays the important role in flame propagation. In this chosen region the flame is thought of as advancing by a random walk relay race. As one group of molecules reacts and liberates its heat it sets the stage for an adjacent group which, by means of a random walk of n free paths, completes its lap in the relay race by releasing its energy. The flame velocity is determined by the value of n which is a collision rate divided by a reaction rate, both determined at the point of maximum reaction velocity.

DIESEL COMBUSTION

Infra-red spectroscopy has been used for the first time in the study of combustion in the diesel engine, by W. T. LYN, in the laboratories of the British Internal Combustion Engine Research Association and this work was described in a paper presented in September to the Institute of Petroleum. Emission spectroscopy was used as there were considerable practical difficulties in applying absorption spectroscopy, although this is to be preferred from the point of view of quantitative interpretation of results. Particular phases of the combustion period were selected for examination, one at a time, by a mechanical strobometer. The spherical combustion chamber of a Ricardo Mk II Comet design was used for the investigation and a Hilger D264 large aperture infra-red spectrometer. Both gas oil and residual blend fuel were used.

Comparison of the engine spectra with those from laboratory flames and from the spark-ignition engine indicates that during the main combustion period in the diesel engine the fuel burns essentially as a diffusion flame. This is evidenced by the strong carbon continuum in the diesel engine spectra which is hardly observable in petrol engine spectra and spectra of

premixed laboratory flames. The extent of carbon formation in the diesel engine is comparable to that of a diffusion flame of acetylene, and there is a striking similarity in the two spectra.

In the engine, the effect of pressure is pronounced. The higher pressure occurring in an engine greatly facilitates and accelerates the pyrolysis of hydrocarbons to such an extent that carbon formation takes place before the fuel has an opportunity to mix intimately with air. A certain amount of pyrolysis takes place during the delay period. The type of original fuel, whether distillate or residual, almost certainly determines the structure and reactivity of the solid intermediates which arise from partial oxidation and polymerization of the carbon formed by pyrolysis.

The present investigation emphasizes that pyrolysis under high pressure leading to carbon formation is the crux of the combustion problem in diesel engines, at least from the chemical point of view.

VISCOSITIES OF GASES AT HIGH TEMPERATURES

Knowledge of the high temperature viscosity of the products of fuel combustion is essential for the purpose of heat transfer calculations for boilers, jet engines and gas turbines. Experimental data available on this subject up to the present time have been comparatively few. M. J. KENNEY, R. J. SARJANT and M. W. THRING, University of Sheffield, have recently described an apparatus which was used to determine the viscosity of mixtures of gases up to temperatures of approximately 900° C. [*Brit. J. appl. Phys.* 7 (1956) 324].

The apparatus was based on the design of R. S. EDWARDS [*Proc. roy. Soc. A* 117 (1927) 245], the gas being heated to the operating temperature in the same furnace as the capillary tube, so as to overcome an objection to the capillary flow method that the gas entering the tube was not at the temperature of the tube. The method consists essentially in observing the rate of fall of gas pressure in a closed, heated container over a short period during which the gas is flowing out to the atmosphere along a heated capillary tube. Viscosities of various mixtures of carbon dioxide and nitrogen were determined up to 900° C. A comparison between the experimental values obtained and those calculated for similar gas mixtures on the basis of modern theory of transport coefficients, shows that it is possible to calculate the viscosities of gas mixtures at high temperatures with an accuracy of at least 2 per cent.

MODELS FOR OPEN-HEARTH FURNACE RESEARCH

A comprehensive survey of Russian research into the behaviour of gases and flames in open-hearth furnaces has been given by Professor M. A. GLINKOV, of Moscow, in a review presented to the Société de l'Industrie Minérale in Paris (translation by R. SEWELL, of Swinden Laboratories, United Steel Companies Ltd.) [*Iron Coal Tr. Rev.* 173 (1956) 89].

Water and air models have been used for a considerable number of years in Russian research to investigate the mixing of gases in furnaces. Recently, in addition to measuring concentrations, the so-called 'without inertia'

method has been used which consists of adding common salt at different points. Measurements of electrical conductivity are made using alternating current. This method has the possibility of giving the true field of concentrations conditioned by the presence in the current of turbulent pulsations, as compared to the statistical mean values obtained by the ordinary method of sampling [S. M. ANDONIEV, O. V. FILIPIEV and E. V. POPOVA, *Stal* No. 1, 1955].

The use of models for studying open-hearth furnace problems was one of the main themes at the Forty-sixth Steelmaking Conference, organized by the British Iron and Steel Research Association at Ashorne Hill in August 1956. The opinion was expressed by J. H. CHESTERS, of the United Steel Companies Ltd., that the end of the first stage of model work, that of achieving similarity in the model, was now within sight. In the next stage, of application of the results of experiments in models to full-scale furnaces, one of the important decisions to be made is as to what character of flow pattern is desirable. Descriptions of research into design and operation of open-hearth furnaces using models were given by W. P. CASHMORE, of the Guest Keen Iron and Steel Company, by A. E. PEARSON, of Dorman Long (Steel) Ltd., by E. H. HUBBARD, J. VAN LANGEN and M. RIVIÈRE, who described work by the International Flame Research Foundation at IJmuiden, and R. MAYORCAS, of the Steelmaking Division of the British Iron and Steel Research Association. It is proposed to do work in the BISRA's Sheffield laboratories on a hot model in order to investigate radiation characteristics of flame and convectional heat transfer to a hearth [*Iron Coal Tr. Rev.* 173 (1956) 383].

Three recent communications of original investigations in this field witness to the increasing importance of this subject. Two papers are from the Aerodynamics Laboratory of the Research and Development Department, The United Steel Companies Ltd., and the third from the Department of Fuel Technology and Chemical Engineering, University of Sheffield. In the first of two papers by F. A. GRAY and A. D. ROBERTSON [*J. Inst. Fuel* 29 (1956) 424, 428] a description is given of model techniques using air for studying fluid flow problems. After describing the laboratory and equipment, the techniques are illustrated by typical examples of problems investigated: flow distribution in pipes and furnaces, mixing and entrainment, flow of particles in gas streams, flow in granular beds, and the calibration of metering devices. In their second paper the authors describe the use of model techniques to obtain a simple relationship on which to assess the effect of buoyancy in furnaces from tests on hot air discharged horizontally from circular orifices into air at room temperature. An empirical relationship has been derived which can be used as a first approximation to indicate the error introduced by neglecting the effect of buoyancy in isothermal models.

In the third paper, G. HORN and M. W. THRING [*J. Inst. Fuel* 29 (1956) 437] describe work which had for its objective the development of a technique for introducing buoyancy effects into models of furnace systems. The cold type of furnace model was used, as this does not introduce the complication of the mechanism of combustion, nor does it require heat-

resisting materials. It also allows transparent components to be used and so makes possible direct visualization of the flow patterns. Liquids or gases can be used to represent the flow of fuel gas and air for combustion. The essential requirement is that of dynamic similarity which is obtained by equality of Reynolds and Froude numbers. The decision to use a water model was taken in view of the fact that the velocity of air required would be over 10 times that of water in order to produce the same Reynolds number in a model of the same linear scale, since the kinematic viscosity of cold air is more than 10 times that of cold water. The lower velocities in water are more satisfactory for the purpose of visual observation.

In this work a jet of slurry was used which being denser than the surrounding water sank and so provided an inverted representation of a rising flame jet. The material used to make the slurry was crushed magnetite, having a specific gravity of about 4·5 and could be made up into slurries having a range of specific gravities up to about 2·5.

STUDY OF KNOCK BY KINETIC SPECTROSCOPY

An important investigation on the mechanism of knock and anti-knock has recently been described by K. H. L. ERHARD and R. G. W. NORRISH [*Proc. roy. Soc. A* 234 (1956) 178]. The experimental method of flash photolysis was used to ignite mixtures of acetylene, oxygen and amyl nitrite in a reaction vessel 50 cm long by 2 cm diameter, and the course of the explosive combustion was followed by flash spectroscopy and by photo-electric technique. These experimental methods had already been applied successfully to combustion [R. G. W. NORRISH and G. PORTER, *Nature, Lond.* 164 (1949) 658; *Proc. roy. Soc. A* 210 (1952) 439; G. PORTER, *Proc. roy. Soc. A* 200 (1950) 284; R. G. W. NORRISH, G. PORTER and B. A. THRUSH, *Proc. roy. Soc. A* 216 (1953) 165; *Fifth Symposium on Combustion*, p. 651, Reinhold Publishing Corporation, 1955]. Amyl nitrite was chosen as it is a strong pro-knock and therefore might be expected to produce a very rapid auto-ignition, and at the same time it also served as a sensitizer, as no other substance was found which could be photolyzed so readily and was chemically so inert as not to react with lead tetraethyl on mixing.

It was found that two phases could be distinguished in the explosion: (*i*) an induction period following the immediate disappearance of the spectrum of amyl nitrite during which no radical spectra were visible; (*ii*) a fast build-up of diatomic radical spectra, chiefly OH, with a little NH and CN, at the point of ignition accompanied by strong light emission upon which were superimposed high-temperature emission peaks of only a few microseconds' duration, indicating strong compression or detonation waves travelling through the reacting gases.

On adding small amounts of lead tetraethyl the induction period was greatly lengthened; 0·2 mm (Hg) of lead tetraethyl increased phase (*ii*) up to 200 per cent and the strong emission caused by heavy detonation was often completely quenched. It was established that the anti-knock effect of lead tetraethyl is a completely homogeneous gas-phase reaction and the

early suggestion of A. C. EGERTON [*Trans. Faraday Soc.* 24 (1928) 697] that the anti-knock substance must be oxidized and molecularly dispersed in order to be effective is strikingly verified by this work.

DETONATION OF METHANE

ELWYN JONES has recently put forward a possible explanation of the fact that the equimolecular mixture of methane and oxygen is that most readily detonated of these two gases [*Nature, Lond.* 178 (1956) 1112]. With the simple paraffin hydrocarbons including methane, the most reactive mixtures with oxygen are those in the molecular proportion 2 : 1, although none of these mixtures can propagate flame at normal temperature and pressure. It is suggested that, thermodynamically, the determining step in the slow combustion of methane involves two molecules of methane and one of oxygen. The slowness of the reaction probably indicates the low frequency of such a three-body collision process. The simplest re-arrangement of this tri-molecular grouping would appear to involve the initial formation of methyl alcohol and this would accord with W. A. BONE'S scheme for the slow oxidation of methane.

Jones suggests that a two-body collision process is the initial one in the detonation of the equimolecular mixture of methane and oxygen. A molecule of each kind may be involved and, as the products are $CO + H_2 + H_2O$, the methane molecule divides and since three new molecules are formed it must divide into three. Consequently much more energy per mole is required to trigger detonation than slow combustion.

It is suggested that in deflagration there are two successive bi-molecular encounters involving first one oxygen molecule (an event distinguishable from detonation) and then the other. The activation energy of the whole process may correspond to that of the first stage whereas the total energy released is the sum of the two stages. Thus the energy released in detonation may represent only part of the total energy available and may be much less than that generated by deflagration. If so, the violence of the detonation process must be attributed more to the speed of reaction than to the amount of energy released and this depends on the statistical frequency of encounter between the appropriate species. Jones suggests that this probably explains why the maximum detonation velocity in methane–oxygen mixtures occurs not in the stoichiometric but in the equimolecular mixture.

CONTROLLED BURNING OF COMBUSTIBLE MATERIALS

A simple, rapid method has been described by A. SCHRIESHEIM for burning combustible materials under closely controlled conditions [*J. Res. nat. Bur. Stand.* 57 (1956) 245]. A given quantity of material can be burnt in a fixed amount of air at a selected initial temperature, and the gaseous products can be collected and analysed. The equipment consists essentially of a combustion chamber containing a heating element for firing the specimen, and apparatus to control the amount of air in the chamber. The combustion chamber is a 2 l. *Pyrex* flask containing a silica tube in which the specimen is placed.

In use, a porcelain boat containing the material to be burnt, is placed in the silica tube as far from the platinum heating coil as possible. The combustion chamber is evacuated, and a controlled amount of air is admitted. Current is applied to the heating coil until the desired firing temperature is reached. On inclining the combustion chamber, the boat slides down into the heating coil and burning begins. After the temperature has been kept constant for the appropriate time, the current is switched off and the apparatus allowed to cool. The combustion gases are then available for analysis in a mass spectrometer or by other methods.

HIGH INTENSITY COMBUSTION

R. P. FRASER, of the Imperial College of Science and Technology, London, recently presented a paper to the Institution of Chemical Engineers, on the significance and advantage of burning fuels at high rates of volumetric heat release [*Engineering, Lond.* 183 (1957) 20].

The burning of liquid fuels, both distillates and residual fuels, under high intensity conditions as in the jet aero engine, is now receiving increasing attention as regards discovering the best practical equipment and optimum conditions obtainable. The author discussed particularly the limitations in the design of existing combustion chambers. In burning fuels in suspension in the form of particles, there is an obvious complex dependence of the volumetric heat-release rate on the physical and geometrical character of the burning mixture. Large particles moving at a low velocity relative to the air will have only limited contact with oxygen. Because of their large mass, such particles plus their gas envelopes occupy only a small fraction of the mixture volume. To obtain a large interface between fuel and oxygen requires that the fuel particles be very small. How heat-release rate depends on the mean particle size still requires to be determined.

The character of the combustion chamber walls is an important factor. Heat absorption by metallic walls, detrimental to the rate of burning by cooling the flame, can be reduced by ceramic linings if these are of a character to allow them to attain temperatures more nearly that of the flame. Moreover, hot walls can produce stabilization of combustion at much higher mass velocities without blowing out, and consequently much greater combustion intensity can be maintained.

As regards combustion chamber design, industrial equipment differs according to whether the exhaust jet velocity or the gaseous product composition is important; the devices for the former are usually referred to as thermal jet burners and for the latter, high intensity or high duty combustion chambers. Examples of combustion chambers using gaseous fuel and designed to give high heat-release rates are those using a ram jet apparatus, pulsating combustion, or a partially submerged burner for heating liquids. Combustion chambers for liquid fuels may be of the 'jet-can' variety for aero gas-turbines, those using a chamber with space for atomization from a vaporizing-tube wall, or those using a hollow spray cone, with or without separate zones of secondary air.

There is now a trend away from the large refractory brick-lined furnace as a heat source of combustion at high volumetric rates, in favour of high intensity burners. These are compact, light in weight, mobile, and allow the heat to be applied directly to the object to be heated. Although the operation of high velocity thermal jets entails the use of a comparatively large amount of energy, the capital cost of the complete plant is usually less than that of large refractory-lined furnaces.

COMBUSTION SYMPOSIUM

The Sixth International Symposium on Combustion sponsored by the Combustion Institute was held at Yale University on 19 to 24 August 1956.

One of the outstanding papers dealing with fundamental concepts in the theory of flame was presented by T. VON KÁRMÁN. His subject was the present status of the theory of laminar flame propagation. He summarized the position by saying that the theory has been based on applying equations of conservation of mass and energy to a one-dimensional flow of a mixture which is unburnt at the cold boundary and approaches an equilibrium state at the hot boundary. Kármán considers that such a theory is based on assumptions whose validity is in considerable doubt. Some of these assumptions are that the flow can be regarded as that of a continuous gas, that the chemical kinetics furnish the necessary expressions for the chemical changes entering in the conservation equations, and that the transfer phenomena are characterized by full knowledge of the heat transfer coefficients and the laws of diffusion. Further, it is assumed that pressure variations can be neglected. Moreover, when an ignition temperature is introduced into the equations the interpretation to be placed upon this is very uncertain. There is no physical reason for assuming a definite ignition temperature.

D. B. SPALDING, of the Imperial College of Science and Technology, London, in a paper on ends and means in flame theory, points out that if a reaction proceeds by way of a single step, numerical solution is easy but the labour of computation becomes progressively greater as the number of intermediate radicals increases. So far few reactions have been studied that compare in complexity with those which chemists believe obtain in real flames.

A paper on turbulent burning velocities of natural gas–air flames with pipe-flow turbulence was presented by J. K. RICHMOND, J. M. SINGER, E. B. COOK, J. R. OXENDINE, J. GRUMER and D. S. BURGESS, of the U.S. Bureau of Mines, Pittsburgh. This investigation was carried out to test existing theories of turbulent burning velocity and particularly to search for flame-generated turbulence. Measurements were made of burning velocity as a function of height in Bunsen flames. A stoichiometric mixture of natural gas and air was studied at 10000, 25000, 50000, and 100000 Reynolds number of approach flow, with a $1\frac{1}{4}$ in. burner tube. It was found that there was much greater divergence of approach gas flow in the presence of these flames than would exist in a similar flow without a flame, and the flow divergence is always accompanied by an increase in static

pressure which is many times larger than that corresponding to the laminar flame pressure. Flame-generated turbulence, if any, was found to be quite small.

'METHANE AND ITS COMBUSTION'

The recipient of the Melchett Medal of the Institute of Fuel for 1956 was SIR ALFRED EGERTON, F.R.S., Emeritus Professor of Chemical Technology in the University of London. The presentation of the medal was made in April of last year and in November Sir Alfred delivered the lecture associated with the award, taking for his subject, 'Methane and its Combustion' [*J. Inst. Fuel* 30 (1957) 3]. The greater part of the lecture was concerned with limits of inflammability, combustion of methane, and methane as a fuel. Reference was also made to the direct synthesis of methane from carbon monoxide and hydrogen and also the possible use of the Lurgi generator for the production of methane by the hydrogenation reaction.

In the lecturer's discussion of limits of inflammability, results were quoted which were obtained by the use of the flat-flame burner developed in Egerton's laboratories at South Kensington [J. POWLING *Fuel, Lond.* 28 (1949) 25; A. C. EGERTON and S. THABET *Proc. roy Soc. A* 211 (1952) 445]. In this type of burner the gas flow is divided into a very large number of little tubes. After emergence the flow coalesces and a uniform velocity distribution is established across the wide burner and the result is a flat disk of flame. This flame is the nearest type to compare with the theoretical concept of flame. With this burner flame was found to maintain itself with rather weaker mixtures than would propagate in tubes, but there was still a limiting composition below which flame could not be maintained as a stable flat flame. The theory for steady state flame propagation, with a term to include the over-all reaction kinetics, includes nothing which would predict a limiting burning velocity. It must be allowed that some special behaviour is characteristic of flame reaction which does not influence the steady conditions of flame propagation, but only becomes important for mixture compositions near the limits, or for ignition and other unsteady state conditions. Whether or not experimentally determined limits of inflammability are true limits or are only apparent limits due to mechanical effects, is at present undecided.

Dealing with the combustion of methane, the lecturer began by reference to the work of J. H. BURGOYNE and H. HIRSCH [*Proc. roy. Soc. A* 227 (1954) 73] in the Imperial College laboratories on the problem as to whether methane at low concentrations in air, 0·5 to 1 per cent, could be burnt at high temperature rapidly and completely. It was found that these weak mixtures, which are well below the weak limits at ordinary temperature, burn rapidly if the temperature is high enough, 950 to 1000° C. An interesting observation was that the carbon monoxide formed in the oxidation of methane does not burn until all the methane has been burnt: methane inhibits the oxidation of the carbon monoxide. There are two stages in the combustion process. Formaldehyde, which is the first intermediate stable product, is the agent inhibiting the carbon monoxide

oxidation. The oxidation of hydrogen goes along with that of methane and is not inhibited as is that of the carbon monoxide. In Burgoyne and Hirsch's experiments the methane and air were separately heated and flowing at high speed were fed together, at known rates to give the right mixture, into the small reaction space maintained at a constant temperature. These experiments are of particular interest in connection with combustion in fast air streams which is so important in relation to combustion systems in jet aero engines.

The process by which methane oxidizes was discussed. The considerable amount of research during the past fifty years on the slow oxidation of methane has not led to a generally accepted view as to the chemical mechanism involved. Egerton drew attention to the scanty analytical work in these investigations which have mostly relied on following the rates of over-all pressure change. Such pressure change is the net result of a number of simultaneous and consecutive chain reactions and may be of little value unless substantiated by sufficient analytical data. In his most recent work on the subject Egerton has analysed the products of oxidation at various stages of the reaction as well as following the rate of pressure changes [A. EGERTON, G. J. MINKOFF and K. C. SALOOJA *Proc. roy. Soc. A* 235 (1956) 158]. Mixtures of methane and oxygen were studied between 440° and 520° C, and 100 and 350 mm Hg pressure. When reacting in *Pyrex* vessels freshly cleaned with hydrofluoric acid, the mixtures were found to behave in a reproducible manner. Formaldehyde was found to be formed from the beginning of the reaction, including the induction period. Its concentration reaches a maximum near the stage where the pressure rise is a maximum, and then falls off. Hydrogen peroxide is also formed, less rapidly in the earliest stages but its rate of formation overtakes that of formaldehyde and it reaches an even higher concentration. It is suggested that the hydrogen peroxide is formed by means of HO_2 radicals arising from the oxidation of the formaldehyde. No other peroxides were detected and no methanol was found. Hydrogen was present in the gaseous products. These observations do not agree in some respects with certain conclusions from earlier investigations. Later work on the effects of surfaces and of inert gases is to be reported before the mechanism of the reactions is discussed, since the surface under the conditions used determines the reaction behaviour.

W. A. KIRKBY

Publications

SELECTED COMBUSTION PROBLEMS II

Transport Phenomena; Ignition; Altitude Behaviour and Scaling of Aeroengines

Advisory Group for Aeronautical Research and Development, North Atlantic Treaty Organization. London: Butterworths Scientific Publications, New York: Interscience, 1956. *vii* + 495 *pp.* 90*s.* $12.50

THE publication of the second volume of *Selected Combustion Problems* makes available the proceedings of the combustion colloquium held under the auspices of the Advisory Group for Aeronautical Research and Development at Liége, Belgium, in December 1955.

Since, quoting from the introduction, 'more national and international combustion meetings were held during 1955 than in any year in history,' and since, on present form, it seems likely that even this record will not long remain unchallenged, it is perhaps worth re-stating that the special aim of these meetings lies ultimately in aeronautical applications. It was felt by the organizers that the previous Cambridge meeting contributed greatly to the practical development of this subject and that the published proceedings (*Selected Combustion Problems—Fundamentals and Aeronautical Applications*) aroused such widespread interest that a second colloquium seemed desirable.

Eighteen papers were presented at the colloquium. These have been sub-divided under five headings with some degree of inevitable overlap between sections. As in the earlier colloquium, the procedure was followed of presenting papers at the rate of three or four each morning, the afternoons being devoted entirely to their discussion. The contributions to these discussions, sub-divided under the titles of the papers to which they refer, are presented at the end of each section of the book, together with the authors' replies.

The first section, entitled 'Aircraft Engines and Fuels', consists of two papers, each of which deals with one aspect of the section heading. The contribution on aircraft engines is concerned primarily with the criteria of engine performance. It examines in detail the relative merits of thrust and power in terms also of fuel consumption, weight and other parameters and relates these to practical requirements of optimum performance under various conditions. The second deals with properties of turbojet fuels and presents an excellent summary of physical and chemical requirements. Stability in storage is omitted. The assessment of actual fuels is confined largely to those grades meeting U.S. military fuel specifications. Rapid developments in aircraft performance and engine design may necessitate some revision of the conclusions in future.

The four papers of the second section, entitled 'Ignition and Flammability', illustrate the fact that although ignition criteria were among the first combustion properties to be studied they are still far removed from an ultimate analytical solution. The first paper constitutes a re-statement of the 'excess enthalpy' hypothesis, the second deals with ignition of flowing gases, the third with that of liquid propellants and the last presents a review of ignition by temperatures in excess of 'auto-ignition' temperatures and the time delays involved, including both empirical results and their theoretical treatment by thermal and 'radical chain' mechanisms. The subsequent discussion echoes the controversial nature of the subject.

The third section, 'Transport Properties', consists of three papers, the first of which compiles the underlying fundamental relationships, including equations of state and enthalpy, transfer coefficients in pure gases and mixtures—diffusion under pressure and temperature gradients is considered in addition to those of concentration.

The fundamental conservation equations are re-stated in the general case and reduced finally to that of the one dimensional stationary process. The second contribution deals with convection at high speeds and elevated temperatures beyond the range covered theoretically by present knowledge. By somewhat extended extrapolation, rules are suggested for the approximate calculation of coefficients from low temperature, low velocity data. The last paper gives a very comprehensive review of sources of transport coefficients and correlation of thermodynamic and transport data. This includes a catalogue of recent compilation reviews, an indexed bibliography of research on transport properties (1945 to 1954) and a list of ranges of a number of publications. Suffice it to say that the survey of literature under the several headings totals 556 references. A contribution in the discussion considers the extension of the theory of transport coefficients to temperatures above 1500°K.

Of the four papers constituting the section on 'High Altitude Combustion Problems', the first three deal with the application of theory and experimental data—including data obtained under small-scale and laboratory conditions, occasionally in very different systems, *e.g.* laminar burning velocities and ignition-lag data—to practical aspects of turbojet combustion chambers such as stability, re-lighting and efficiency. Scaling, approaches by way of an 'over-all reaction' and dimensionless correlations are considered in the theoretical developments. The fourth contribution employs laboratory data on pre-mixed and diffusion flames to examine the question of the existence of an absolute limit of inflammability at low pressures, divorced from quenching effects and their increased importance at reduced pressures.

The final section, 'Similarity, Scaling and Fundamental Parameters', comprises five contributions, two of which deal with rocket motors. Several of the papers contain reviews of the similarity parameters involved and their respective relevance under varying conditions and magnitudes to the individual processes which together constitute the operation of a combustion chamber. If shortage of space justifies somewhat sweeping generalizations it may be concluded that, whilst comprehensive scaling in a perfectly general system is not possible, reasonable compromises and good approximations are possible in particular practical cases. Twenty-one pages of discussion testify to the interest aroused by the section.

A new feature of the colloquium was the insertion of a session devoted to films dealing with intrumentation and a brief summary of these concludes this volume.

Of the eighteen papers presented five (one in each section) are in French and both French and English papers carry summaries in translation. Many of these are rather too brief to be informative. The book is provided with a subject index and is produced with the excellence we have come to expect from its publishers.

Although there now seems to be a clearer understanding of some of the fundamental processes, the second A.G.A.R.D. colloquium, like its predecessor, is to be regarded, not as providing final answers in the domains considered but rather as a statement and attempt at integration of present knowledge. The fact that eighty-one pages are devoted to discussion contributes to the achievement of this aim and tends to elevate the publication above being merely an occasional vehicle for original and review papers.

In this, and in its compact concentration on a few selected topics of particular relevance to aeronautical applications, it makes a very real contribution and will, in the opinion of the reviewer, attract as much attention as its predecessor.

F. J. Weinberg

FLOW OF GASES THROUGH POROUS MEDIA

P. C. Carman. London: Butterworths Scientific Publications, 1956. *x* + 182 *pp.* 22 *illustrations.* 30*s*

Research into the reactivity of solid fuel beds has in recent years been directed towards a study of the gas-solid reaction processes and it is fairly well established that reactivity, the temperature coefficient and the kinetic order of a reaction are significantly influenced by mass transfer. Hence an insight into the manner in which

pore structure, particle size, temperature, pressure and surface properties affect mass transfer is of vital importance.

This work constitutes an attempt to provide an integrated and quantitative account of the transport problem when gases flow in the viscous or molecular regimes through porous media and no chemical reaction takes place. Dr P. C. CARMAN, who is well known for his classic contributions to this field over the last twenty years, has produced a valuable summary of the up-to-date state of knowledge on the theoretical and experimental side. The treatment is not broad enough to serve as a general text and a complete understanding of the subject can only be gained by full use of the numerous references. The practical man is likely to feel at home only in the chapter on permeability method of surface area measurement.

Viscous flow in granular and fibrous media is treated with reference to pore shape and size. The myth of the Kozeny 'constant' has been fully exploded and the author has almost succeeded in never calling his k a constant. The derivation of the Kozeny equation for granular media, although of necessity very brief, is invaluable for an understanding of the tortuosity considerations. A derivation of the Kozeny equation for fibrous masses, equation 1·61 would have been helpful too since without it the use of Table 6 and particularly the deduction that $k \simeq 6$ for $\varepsilon < 0{\cdot}8$ needs further elaboration.

The two chapters on slip flow, free molecular flow, diffusional flow, and the flow of sorbable gases are excellent and are to be recommended for the study of the transport problems occurring in reaction processes in spite of the limitations of the treatment to mass transfer without simultaneous heat transfer and chemical reaction. It contains the first summary of an analytical treatment of surface diffusion in the adsorbed layer which takes place in addition to diffusion or flow in the gas phase. Under suitable conditions surface diffusion can account for a considerable portion of the transport, *e.g.* about half the flow of carbon dioxide through activated carbon takes place by this mechanism. The author expects the surface diffusion of chemiadsorbed gases in porous media to play an important role in porous solid catalysis, but only refers to chemisorption briefly for lack of published experimental studies.

The book ends with a descriptive chapter on the separation of gas mixtures and a brief cursory treatment of the transition to turbulent flow and fluidization. Since separation of gases or vapours on an adsorbent by flow through a bed of granules either by the methods of adsorption or partition chromatography is likely to become one of the most powerful and widely used means of separation not only on a laboratory scale but also industrially, this short account of gas chromatography will be helpful as an introduction. It should make exciting reading for the novice and it is hoped that at a later date the lack of theoretical treatment can be made good. There has been a spate of publications on this subject since this book went to press and one is tempted to mention the Symposium on Vapour Phase Chromatography organized by the Institute of Petroleum in May 1956 (Proceedings published by Butterworths) and Courtenay Phillips's introduction to *Gas Chromatography* (Butterworths 1956).

P. EISENKLAM

THERMODYNAMIC FUNCTIONS OF GASES

Volumes I and II

Edited by F. DIN. London: Butterworths Scientific Publications, 1956. Vol. I, *viii* + 175 *pp.* Vol. II, *vi* + 201 *pp.* 63*s* each volume

MANY scientists and engineers will know the experience of searching through many handbooks and journals in an attempt to find reliable tables or charts of the thermodynamic properties of even the common gases. If found, the charts will often be either minute or of doubtful origin and their use may lead to grossly misleading results. To all such seekers the publication of the first two volumes of *The Thermodynamic Function of Gases* under the editorship of Dr. F. DIN of the British

Oxygen Company will come as most welcome news. The first volume covers ammonia, carbon dioxide and carbon monoxide whilst the second includes air, argon, acetylene, ethylene and propane. The books include a small temperature-entropy chart and tables of properties of the gases together with reviews of the sources of the data, the methods of computation and the probable accuracies of the derived properties. Separate wall charts printed on reinforced paper and measuring about 3 ft × 4 ft may also be purchased.

The charts were prepared in collaboration with the Thermodynamics Committee of the Mechanical Engineering Research Board (D.S.I.R.) although in most cases the actual compilation was done in university or industrial research laboratories.

The first volume includes an excellent introductory article by Din on the assessment of experimental data and the correlations and derivations recommended for obtaining best values of the derived thermodynamic functions (enthropy and enthalpy).

The chart for ammonia was prepared by P. DAVIES of I.C.I. Ltd. and covers the pressure range 0·06 to 1100 atm and temperatures up to 580°K. The charts for carbon dioxide and propane are based on compilations made at Imperial College under Professor NEWITT about nine years ago but with certain refinements subsequently made by H. A. W. HUGGILL and J. S. BATEMAN of D.S.I.R. The data for carbon monoxide were correlated by A. SMEETON LEAH of Leeds University and can only be criticized in that the chart was prepared before the publication of the recent measurements from Amsterdam. Ethylene is dealt with by W. F. L. DICK and A. G. M. HEDLEY of I.C.I., and, partly because of the shortage of low temperature data and partly no doubt because of the restricted range of interest of the authors, does not, unfortunately, extend below 0°C. The remaining diagrams (air, argon and acetylene) were prepared by Din. Of these the air diagram may contain some errors in the critical region because the author has used the Law of the Rectilinear Diameter to correlate the saturated liquid and vapour volumes, which is inadmissible in the case of a mixture.

Considering the series as a whole it is unfortunate that it has not been possible to obtain uniformity of units and that none of the charts is available in normal engineering units. The need to present the correlations in internationally agreed units is obvious so that different charts for the same substances may be compared, however, as no engineer can readily work in Joules or cubic decimeters when his equipment has dimensions and is rated in B.t.u.s and cubic feet. It would seem preferable that M.E.R.B. should complete its excellent work by producing duplicate data in engineering units rather than that each large firm should have to do it separately.

Finally, one might have preferred that each substance was treated in a separate monograph. This is suggested not only for the convenience of the user but also because it is essential that fairly frequent revisions should be undertaken, and one feels that this is less likely with the present collected publications, particularly if only one substance in a book of five requires revision.

These criticisms are, however, marginal and the appearance of these two volumes is indeed good news.

G. G. HASELDEN

Letter to the Editors

Letters to the Editors on points of scientific interest related to combustion and flames are invited. The Editors do not hold themselves responsible for opinions expressed in correspondence. Anonymous contributions cannot be accepted.

Relation of Boundary Velocity Gradient for Flash-back to Burning Velocity and Quenching Distance

THE boundary velocity gradient g, burning velocity u_f and a characteristic distance δ called the 'penetration distance' are related in reference 1 by the equation

$$g = u_f/\delta \qquad \ldots.[1]$$

There are many characteristic distances which have been defined in the literature of combustion such as penetration distance, dead space, flame thickness, quenching distance. K. WOHL[2] has indicated that the over-all behaviour of these distances with pressure, temperature *etc* is parallel Therefore, we can assume that δ is proportional to the quenching distance, d_c, and rewrite equation 1 as follows:

$$g = C\,(u_f/d_c) \qquad \ldots.[2]$$

To check the proportionality of δ and d_c, values of C were calculated from equation 2, using a wide variety of published experimental data[1-12].

It is found that the proportionality factor C is not constant, but increases from 2·5 to 5 as g increases from 10 to 10^5 sec^{-1}. B. LEWIS and G. VON

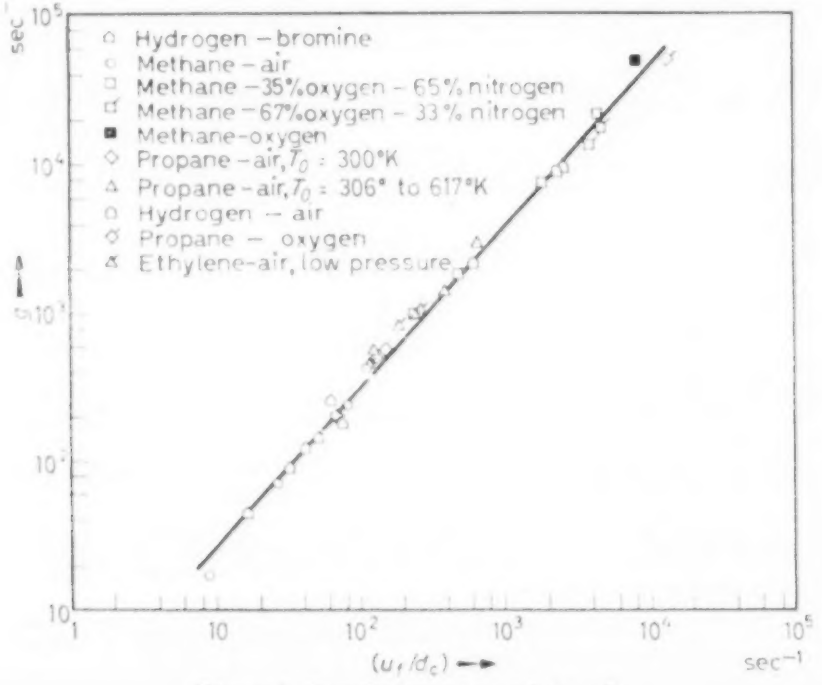

Figure 1. Correlation of g with (u_f/d_c)

ELBE[1] have proposed that the penetration distance should be about half the quenching distance for plane parallel plates. Since this quenching distance is about two-thirds of the quenching distance for cylinders[3] d_c, Lewis and von Elbe imply a value for C of about 3. This is in general agreement with experimental results at g values from 10^2 to 10^3.

The ratio C can be expressed as a constant times g to some power. Then equation 2 can be arranged into a particularly convenient form:

$$g = B\,(u_f/d_c)^{B'} \qquad \ldots . [3]$$

The values of B and B' can be found from a log—log plot of g against u_f/d_c. This plot is shown in *Figure 1*, from which it is found that

$$g = 14{\cdot}125\,(u_f/d_c)^{1{\cdot}168} \qquad \ldots . [4]$$

Because this correlation appears to be quite general—many very different flame types are represented in *Figure 1*—it should prove quite useful for estimation of g, u_f, or d_c for any flame system when two of these quantities are known.

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